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VOL. 14, SEC. A.

NOVEMBER, 1936

NUMBER 11

STUDIES IN THE SPECTRA OF HIGH-FREQUENCY DISCHARGES IN MERCURY VAPOR¹

II. COMPARISON OF ELECTRODELESS WITH EXTERNAL ELECTRODE EXCITATION

III. MODIFICATION DUE TO WAVE-LENGTH

By J. K. ROBERTSON² AND R. H. HAY³

Abstract

High-frequency discharges in mercury vapor have been excited by valve oscillators, and a comparison made of spectra obtained by the use of a purely electrodeless method with those excited by external electrodes. Temperatures ranged from 100° to over 250° C., and the use of four wave-lengths of approximate values 5, 35, 75, and 200 m. made it possible at the same time to examine possible changes in the spectrum arising from changing frequencies. It was found that, with the exception of the highest frequency, external electrodes excitation was more effective for the emission of arc and of spark lines, whereas diffuse bands and regions of continuous spectra could be separated from lines at higher pressures somewhat better by electrodeless excitation.

Evidence is given that the discharge obtained at a frequency of 60 megacycles differs from that obtained at the lower frequencies. At a low vapor pressure a discharge, which is characterized by great brilliance and the absence of spark lines, is obtained with the highest frequency. There is little to choose between the two types of excitation. An explanation is suggested for the difference due to frequency.

Introduction

In a previous paper (8) one of the writers reported the results of an investigation in which the electrodeless excitation of mercury and of cadmium vapors by damped high-frequency currents was compared with similar excitation by undamped currents. In general it was found that at low pressures the bright ring discharge obtained with damped oscillations, by the use of a spark-gap and a condenser discharge, was much more effective in bringing out spark lines than the discharges obtained with valve circuits. The latter means of excitation was more effective at higher pressures for exciting higher members of arc series, and was excellent for bringing out bands and regions of continuous spectra.

In the work of the present paper excitation is produced entirely by the undamped currents obtained by means of valve circuits. Spectra in mercury vapor, excited by a pure electrodeless method (hereafter to be designated *P.E.*), in which the tube containing the vapor is placed inside a coil carrying high-frequency currents (*H.F.*), are compared with those obtained by the

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use of external electrodes (*E.E.*). In the past, care has not always been exercised to distinguish between the two methods, the term *electrodeless* being used sometimes to describe the external electrode method. As the results of this paper will show, spectra obtained by the two methods may differ and it is important to distinguish between the two.

When carrying out this investigation it was possible at the same time to examine possible changes in the spectra arising solely from changes in the frequency of the exciting discharge. In view of the extent to which *H.F.* discharges have been used for the excitation of spectra, the lack of exact information on this particular point is surprising. Ponte (7) in a letter to "Nature" states that he was unable to observe any modification in the spectrum due to a change in wave-length, and considers that any apparent effects of that kind are due to alterations in intensity of the exciting currents or to pressure changes. He, however, used wave-lengths ranging only from 1.9 to 10 m. More recently Bhatt (1), in an investigation comparing the ordinary d-c. arc spectrum of mercury with that obtained by *H.F.* excitation, in which the wave-lengths ranged from 1.5 to 50 m., concludes that "no modification in the *H.F.* spectrum of mercury vapor has been obtained which could be attributed to the variation in the frequency of the exciting system." In spite of this statement, in another part of his paper reference is made to the fact that the intensity of $\lambda = 4797\text{\AA}$ for an exciting wave-length of 20 m. differs from that obtained with other frequencies. In the work reported in this paper, mercury vapor was excited by *H.F.* discharges having wave-lengths of approximately 5, 35, 75 and 200 m. Evidence has been obtained that the spectrum of the discharge excited by the highest frequency differs from the spectra due to the lower frequencies.

Experimental

For all frequencies except the highest, a modified Hartley oscillator circuit with an *S.W. 2A* Mullard transmitting valve was used, connections being made as shown in Fig. 1. A quartz tube about 2.5 cm. in diameter and 15 cm.

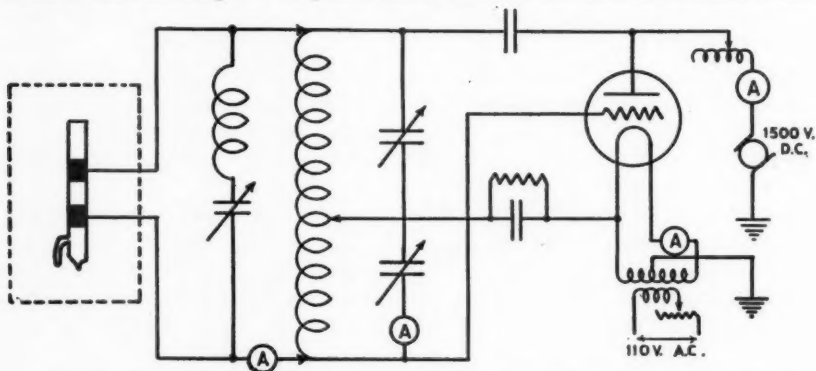


FIG. 1. Diagram of oscillator for wave-lengths 30, 75 and 200 m., with excitation by external electrode.

long, into which a few drops of mercury had been distilled after careful out-gassing by strong preliminary heating, was placed inside an electric oven. The discharge was excited either by four turns of copper tubing wrapped around the tube as in the extreme left of Fig. 2, or by external electrodes as in the extreme left of Fig. 1. The distance apart of the electrodes and the length of the exciting coil were approximately the same (about 3.8 cm.).

For the highest frequency, that is, for the five metre wave-length, a push-pull oscillator with two Western Electric 304A Tubes was used, somewhat as shown in Fig. 2. Currents were read by means of meters placed as shown

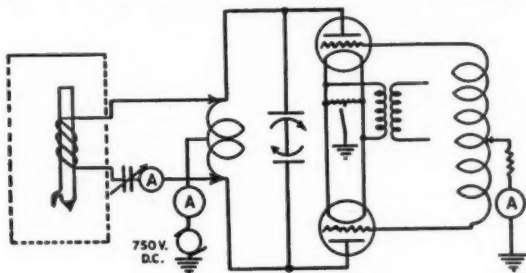


FIG. 2. Diagram of 5 m. oscillator, with excitation by electrodeless coil.

in the diagrams, and an attempt was made to keep values approximately equal in all cases to be compared. As this was not always possible it may be objected that certain conclusions reported in this paper are invalid on that account. Since outstanding differences only are recorded, particularly in the work relating to wave-length changes, it is felt that the conclusions are justifiable.

Spectrograms were taken at temperatures ranging from 100° to 260° C. with a medium-sized quartz spectrograph, Hilger 315E, and, with one or two exceptions, Ilford special rapid panchromatic plates were used.

Results

In comparing *P.E.* with *E.E.* excitation an examination was made of: (i) the general intensity of arc lines; (ii) the presence of certain higher series members; (iii) the presence of spark lines; and (iv) the intensity of regions of continuous spectra and of diffuse bands such as the group in the neighborhood of $\lambda = 2345\text{\AA}$. Typical spectrograms for 5 and 200 m. wave-lengths are reproduced in Plates I and II respectively. It will be observed that the spectra, obtained at approximately equal temperatures, are reproduced in pairs, the top member of each pair corresponding to *P.E.* excitation and the bottom member to *E.E.* excitation. In Plate I, for example, 1 and 2 correspond to *P.E.* and *E.E.* at 100° C.; 3 and 4 to *P.E.* and *E.E.* at 142° C. An examination of these spectra and others for intermediate wave-lengths (not reproduced) gives the following information.

1. (a) For the highest frequency ($\lambda = 5$ m.) and lowest temperature, arc lines are emitted with approximately equal numbers and intensities in both

P.E. and *E.E.* excitation, whereas for lower frequencies, particularly for $\lambda = 200$ m., *E.E.* excitation brings out many more lines than *P.E.* Compare, for example, 1 and 2, Plate I, with 1 and 2, Plate II.

(b) At higher temperatures and shortest wave-length, *E.E.* excitation is slightly more effective than *P.E.* excitation; for $\lambda = 75$ m. not much difference was observed; but for the 200 m. discharge *E.E.* excitation is distinctly more effective for the emission of arc lines.

2. In Plate I, 3 and 4, a group of regularly spaced lines with decreasing intervals may be observed immediately on the short wave-length side of the broadened resonance line 2537\AA . These are the higher members of the diffuse series $1^3P_2 - m^3D_3$ ($m = 12$ to 19). Higher members of the sharp series $1^3P_2 - m^3S_1$ ($m = 12$ to 15) lie in the same region, although not in these particular spectra. With respect to these wave-lengths the writers' results show the following.

(a) The higher members of both series were either absent or very faint for *P.E.* excitation, except for $\lambda = 5$ m., in which case the diffuse series lines were emitted with marked intensity at 142°C ., and faintly at 180°C . Note again Plate I, 3 and 5.

(b) For *E.E.* excitation, for $\lambda = 200$ m. and a temperature of 110°C ., the sharp series members ($m = 13$ and 14) were much stronger than the diffuse, but at higher pressures, even at 194° and 230°C ., the diffuse series members were present with good intensity. Note Plate II, 8 and 10. For $\lambda = 5$ m. at 100°C ., both sharp and diffuse lines were faint, but the diffuse lines were the stronger, while at 142° and 180°C ., the diffuse members were strong but the sharp members were either faint or absent. Note Plate I, 2, 4 and 6.

It is interesting to note, also, that *E.E.* excitation brought out the higher members of the series $1^3P_1 - m^3D_2$ (in the neighborhood of 2300\AA). The spectral lines were broadened and of considerable intensity, for $\lambda = 5$ m. at 180°C . (Plate I, 6), and for $\lambda = 200$ m. at 230°C . (Plate II, 8), and 260°C . (Plate II, 10). At 230°C . higher members of the series $1^3P_0 - m^3D_1$ may also be observed (in the neighborhood of 2200\AA), although of lesser intensity.

3. In comparing the two types of discharges with respect to their ability to bring out spark lines, use was made of the spark lines of wave-length 2225, 2253, 2262, 2407, 2414, and 2848\AA .

The most important general conclusion to be drawn from the spectrograms is the fact that, *except for* $\lambda = 5$ m., *E.E.* excitation is much more effective for the emission of spark lines than *P.E.* With the latter excitation spark lines are either totally absent, or present only at low temperatures. A glance at the lines 2407, 2414 and 2848\AA , marked with an X in Plate III, will be sufficient to make this conclusion evident. For $\lambda = 5$ m., on the other hand, there is little difference between *P.E.* and *E.E.* excitation.

(4). Regarding the emission of diffuse bands such as the groups with head at 2345\AA , the writers' results show that at lower pressures *E.E.* gives more intense bands than *P.E.*, but at higher pressures there is little to choose

between the two. On the other hand, if at higher pressures such bands are desired in a spectrum as free from lines as possible, *P.E.* excitation is the better means. Note the appearance of the 2345 group and the long continuous tail in Plate II, 7 (*P.E.*, 230° C.).

Modification Due to Frequency Changes

For convenience in comparing the effect of change in frequency, spectra obtained by the use of four different wave-lengths at low temperature are grouped in two sets in Plate III, one set for *P.E.* and the other for *E.E.* excitation. In Plate IV a similar grouping is given for high temperature. An examination of these spectra and of others at intermediate temperatures not reproduced shows that in several respects excitation by the highest frequency ($\lambda = 5$ m.) differs from that by lower frequencies, particularly the spectra obtained at 200 m. Some of these differences have already been indicated, but for convenience they are summarized below.

- (1) For the highest frequency, at low pressure, there is little to choose between *P.E.* and *E.E.* excitation;
- (2) Spark lines are entirely absent or very faint;
- (3) A brilliant dazzling white discharge is obtained. The difference between this discharge and those for the lower frequencies may be realized by noting corresponding exposure times. Thus, for $\lambda = 5$ m. and low temperature, the times are 15 and 20 min. as compared with about two hours for $\lambda = 200$ m.

Discussion

Ponte in his note in "Nature" draws attention to "the exceedingly brilliant electrodeless discharge" obtained with a wave-length of 1.9 m., but considers that his inability to obtain more than one or two enhanced lines was due to the low power of his oscillator. As in the writers' work low-level arc lines for $\lambda = 5$ m. were emitted with intensities approximately equal in one-tenth the exposure time of that used for longer wave-lengths, the writers are of the opinion that there is distinct evidence of a modification in the spectrum arising from change in frequency.

That there should be some dependence on frequency seems highly probable in view of the many investigations which have shown that the conductivity is a function of the exciting wave-length. Braun (3), for example, has shown that the minimum current necessary to maintain a glow depends on the frequency. Stuhlmann and Whitaker (10), using a range of wave-lengths between 200 and 500 m., find variations in visual intensity with exciting wave-length, and Brasefield (2), working with mercury vapor, finds a maximum conductivity for a 20 m. wave-length. It may, of course, be argued that observed spectrum changes result from altered conductivity rather than from changed wave-length, but in the writers' opinion the exceedingly intense discharge with spark lines absent is a true frequency effect, and the following explanation is suggested.

If we assume that in all cases an electron is acted on by a simple alternating electric intensity, its motion is given by

$$m\ddot{x} = Xe \sin 2\pi ft, \quad (1)$$

where X is the maximum electric intensity, f is the frequency, and the other quantities have their usual significance. It follows, by simple integration, on the reasonable assumption that at $t = 0$ the electron is at rest, that

$$\dot{x} = \frac{Xe}{m \cdot 2\pi f} (1 - \cos 2\pi ft), \quad (2)$$

and

$$x = \frac{Xe}{m(2\pi f)^2}, \quad (3)$$

where x is the distance traveled by an electron in a half-cycle, if free to do so.

According to this simple theory, the velocity of an electron at the end of a half-cycle varies inversely as the frequency, and the distance traveled varies inversely as the square of the frequency. If we compare excitation by the 5 m. oscillator with the 200 m., we obtain for the lower frequency a velocity 40 times greater than that for the higher frequency, whereas the half-cycle distance is 1600 times greater. Now at 100° C. the pressure of mercury vapor is 0.276 mm. of mercury and the mean free path (4, p. 208) of an electron, at that pressure and temperature, is of the order of 0.3 mm. It is difficult to state with certainty the values of X necessary to maintain a current in mercury vapor at this pressure, but from an estimate based on the ionizing potential of this element and on data obtained by Brasefield (2), its value may be put between the limits 325 and 10 volts per cm. From Equation (3) it then follows that the distance traveled by an electron in a half-cycle, if it is free to move unhindered, is certainly greater than 1 mm. This means that for all frequencies used in the writers' investigation the average electron does not get a chance to move freely for a half-cycle. Since, however, the value of x for the 5 m. oscillator is 1600 times less than for the 200 m., an average electron, for the higher frequency, must execute a very much greater fraction of its theoretical half-cycle distance than for the lower frequency excitation. With the higher frequency, therefore, there would be a much greater number of impacts capable of exciting low-level arc lines.

It may be objected that the greater velocity acquired by the lower frequency electrons would offset the decreased fraction of the half-cycle distance which they travel. Although this is undoubtedly so to some extent, Equation (2) shows that the rate at which velocity is acquired by an electron, owing to the factor $\cos 2\pi ft$, is less for extremely small values of t . Consequently for the longer exciting wave-length, whose t values are such small fractions of the periodic time, there would be a large number of ineffective collisions.

On the other hand, if we consider the few electrons which travel a distance greater than the mean free path, then undoubtedly these would acquire more energy in the case of the 200 m. excitation than the 5 m., and it is not surprising to find spark lines appearing with long exposures.

It is not easy to explain why *E.E.* excitation is more effective than *P.E.* for the emission of spark lines—again except in the case of the 5 m. oscillator. In some respects it is additional evidence that the origin of the electric intensity acting on a gas or a vapor in a *P.E.* discharge is partly electromagnetic and not entirely electrostatic; this confirms the work of MacKinnon (6), Esclangon (5), Smith, Lynch and Hilberry (9), and others. Since the distance between the end turns of the exciting coil was about the same as that between the external electrodes, a purely electrostatic origin of the electric intensity should bring out spark lines with *P.E.* excitation as readily as with *E.E.*, but this is certainly not the case. The fact that external electrodes are tightly wrapped and the coil loosely wrapped, may, however, partly account for the difference. On the whole the writers are inclined to the view that *E.E.* excitation is more purely electrostatic than *P.E.*, although they can suggest no reason why the two types of discharge differ so little in the case of the highest frequency. It is hoped that a continuation of this work with still shorter wave-lengths will throw additional light on the complex problem of the nature of high-frequency discharges.

References

1. BHATT, N. B. Mem. Ind. Inst. Sci. 1 : 891-904. 1935.
2. BRASEFIELD, C. J. Phys. Rev. 37 : 82-86. 1931.
3. BRAUN, M. L. Phys. Rev. 36 : 1195-1203. 1930.
4. COMPTON, K. T. and LANGMUIR, I. Rev. Mod. Physics, 2 : 123-242. 1930.
5. ESCLANGON, F. Ann. phys. 1 : 267-276. 1934.
6. MACKINNON, K. A. Phil. Mag. 8 : 605-616. 1929.
7. PONTE, M. Nature. 121 : 243-244. 1928.
8. ROBERTSON, J. K. Phil. Mag. 14 : 795-805. 1932.
9. SMITH, H., LYNCH, W. A. and HILBERRY, N. Phys. Rev. 37 : 1091-1101. 1931.
10. STUHLMANN, O. and WHITAKER, M. D. Rev. Sci. Instruments, 1 : 772-779. 1930.

PLATE I

Comparison of excitation by external electrodes with electrodeless. $\lambda = 5$ m.

Electrodeless	External electrodes
1. 100° C. \pm 2°. 15 min.	2. 100° C. \pm 2°. 20 min.
3. 142° C. \pm 3°. 15 min.	4. 142° C. \pm 2°. 15 min.
5. 180° C. \pm 2°. 15 min.	6. 180° C. \pm 2°. 15 min.
7. 220° C. \pm 2°. 15 min.	8. 210° - 220° C. 10 min.
9. 260° C. \pm 2°. 15 min.	No discharge at 260° C.

PLATE II

Comparison of excitation by external electrodes with electrodeless. $\lambda = 200$ m.

Electrodeless	External electrodes
1. 110° C. \pm 3°. 110 min.	2. 111° C. \pm 3°. 120 min.
3. 150° C. \pm 3°. 60 min.	4. 150° C. \pm 3°. 50 min.
5. 191° C. \pm 3°. 18 min.	6. 194° C. \pm 4°. 30 min.
7. 230° C. \pm 2°. 7 min.	8. 230° C. \pm 2°. 10 min.
9. 260° C. \pm 2°. 5 min.	10. 260° C. \pm 2°. 6 min.

PLATE III

Variable wave-length at low temperature.

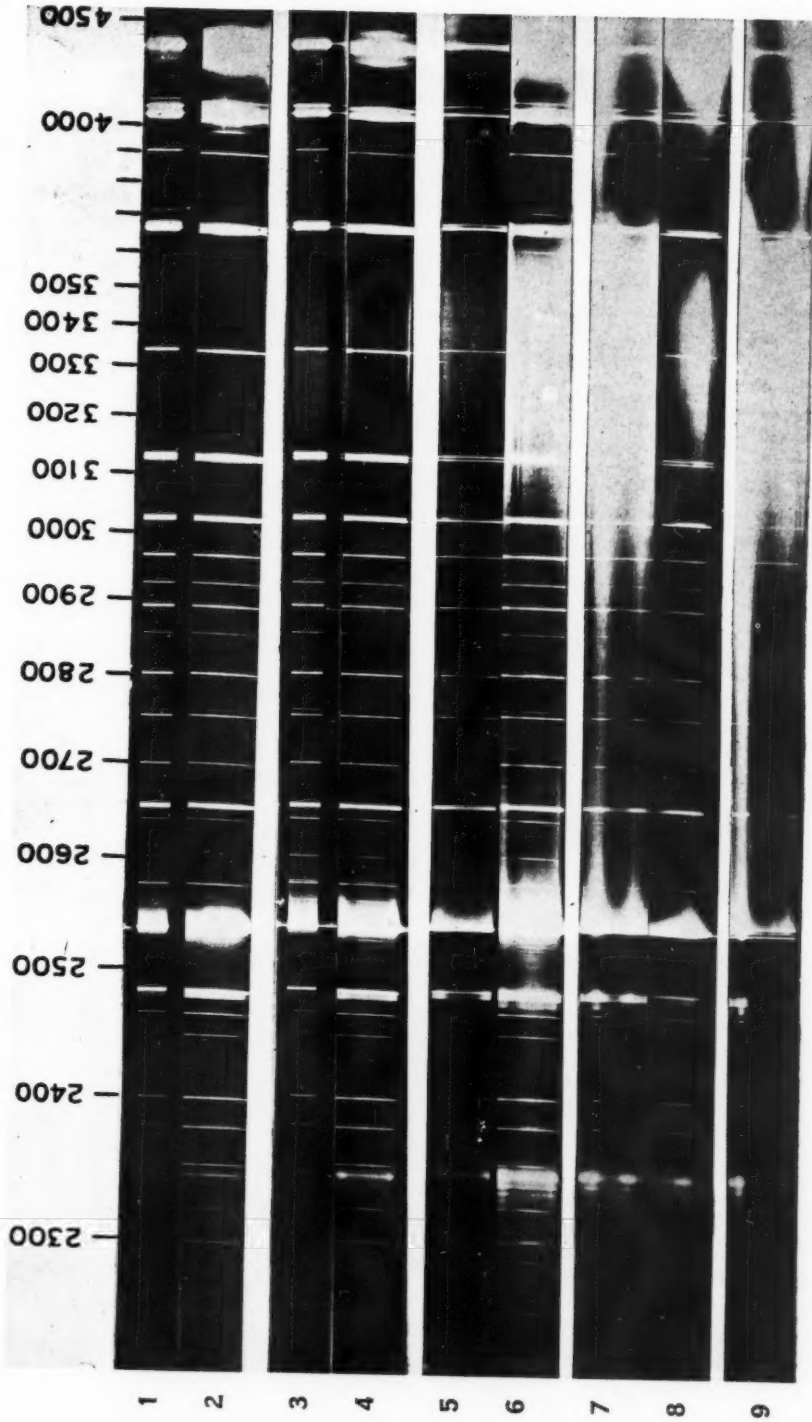
<i>Electrodeless</i>			<i>External electrodes</i>		
1.	5 m.	100° C. \pm 3°. 15 min.	5.	5 m.	100° C. \pm 2°. 20 min.
2.	30 m.	110° C. \pm 3°. 170 min.	6.	34 m.	110° C. \pm 2°. 95 min.
3.	75 m.	110° C. \pm 3°. 130 min.	7.	76 m.	110° C. \pm 2°. 120 min.
4.	202 m.	110° C. \pm 3°. 110 min.	8.	202 m.	111° C. \pm 2°. 120 min.

PLATE IV

Variable wave-length at high temperature.

<i>Electrodeless</i>			<i>External electrodes</i>		
1.	5 m.	220° C. \pm 2°. 15 min.	5.	5 m.	210° C. - 220° C. 10 min.
2.	30 m.	234° C. \pm 2°. 8 min.	6.	34 m.	234° C. \pm 2°. 8 min.
3.	75 m.	225° C. \pm 3°. 10 min.	7.	76 m.	232° C. \pm 2°. 13 min.
4.	202 m.	230° C. \pm 3°. 7 min.	8.	202 m.	230° C. \pm 2°. 10 min.

PLATE 1



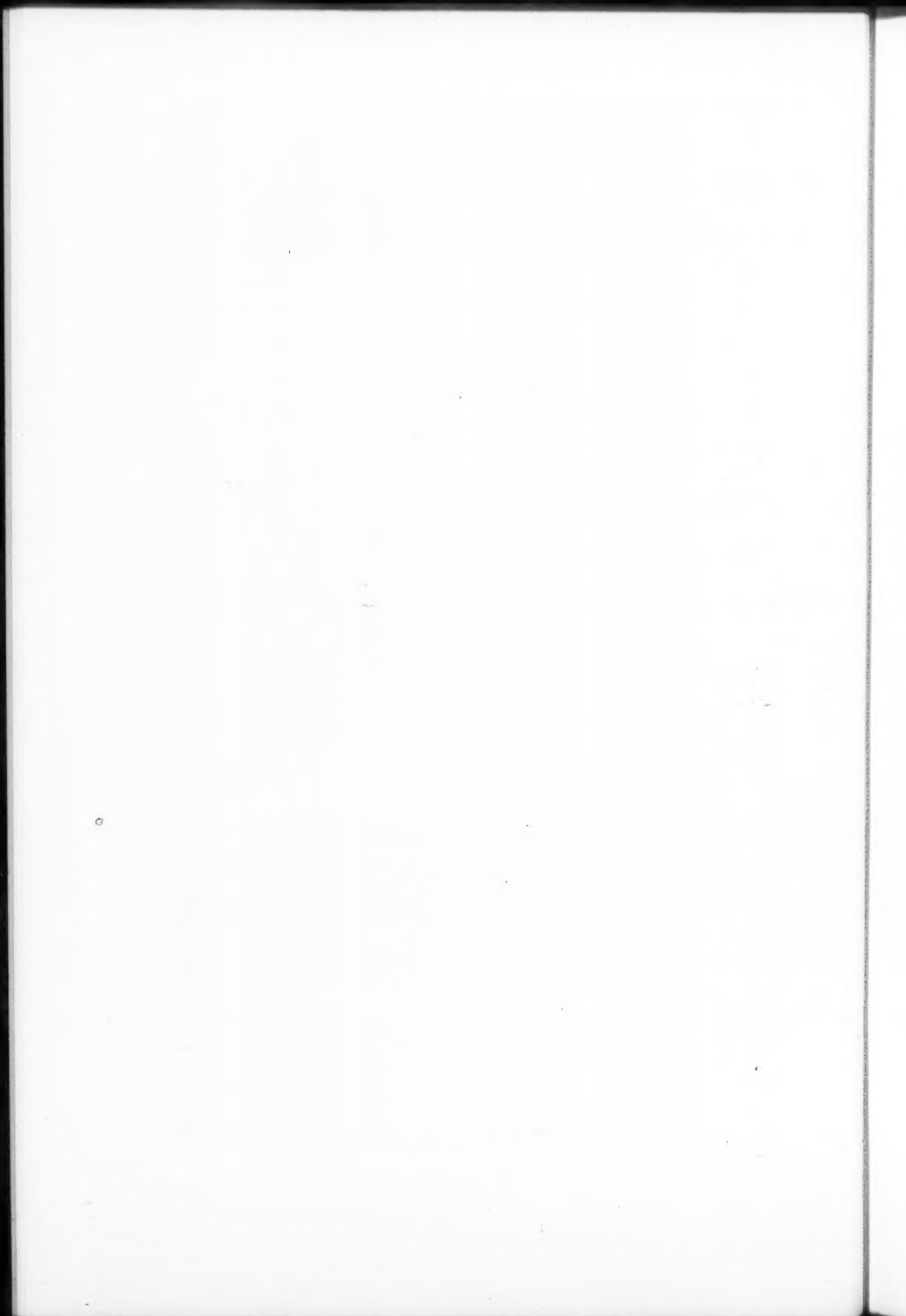
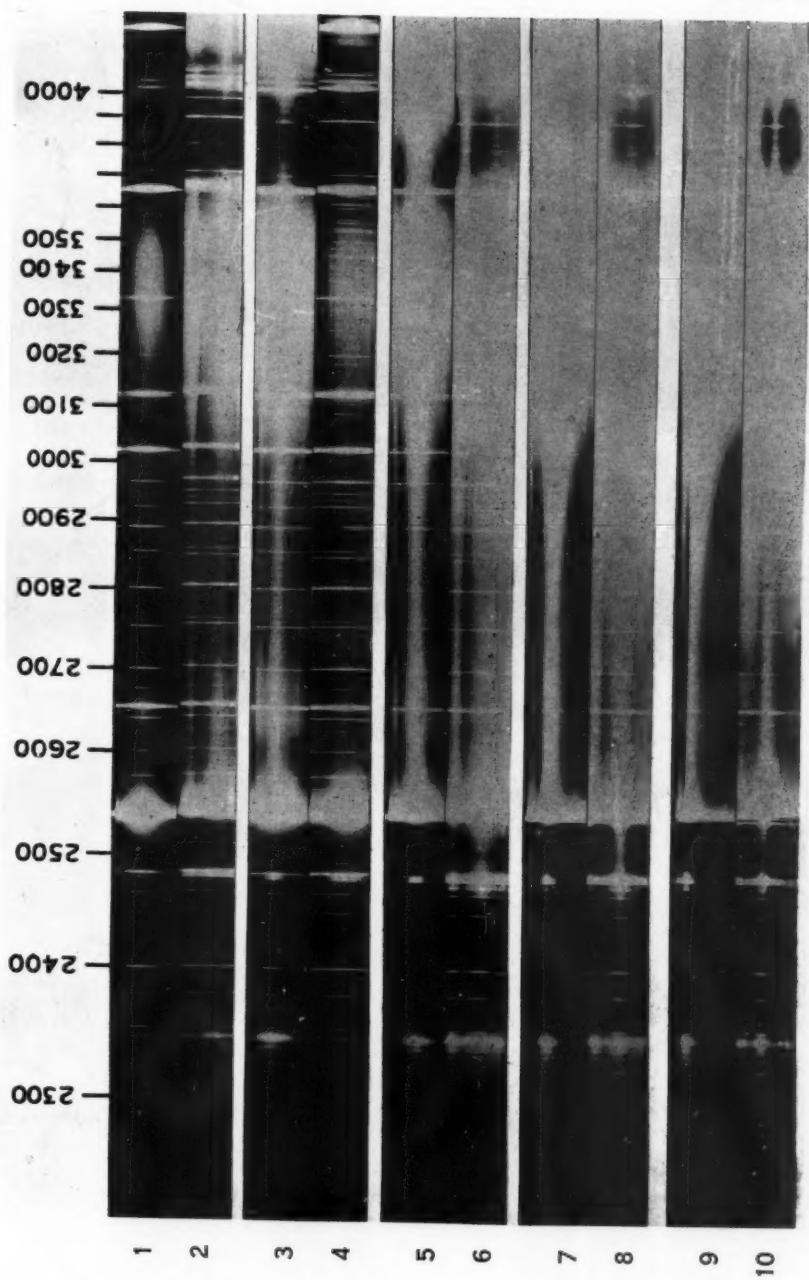


PLATE II



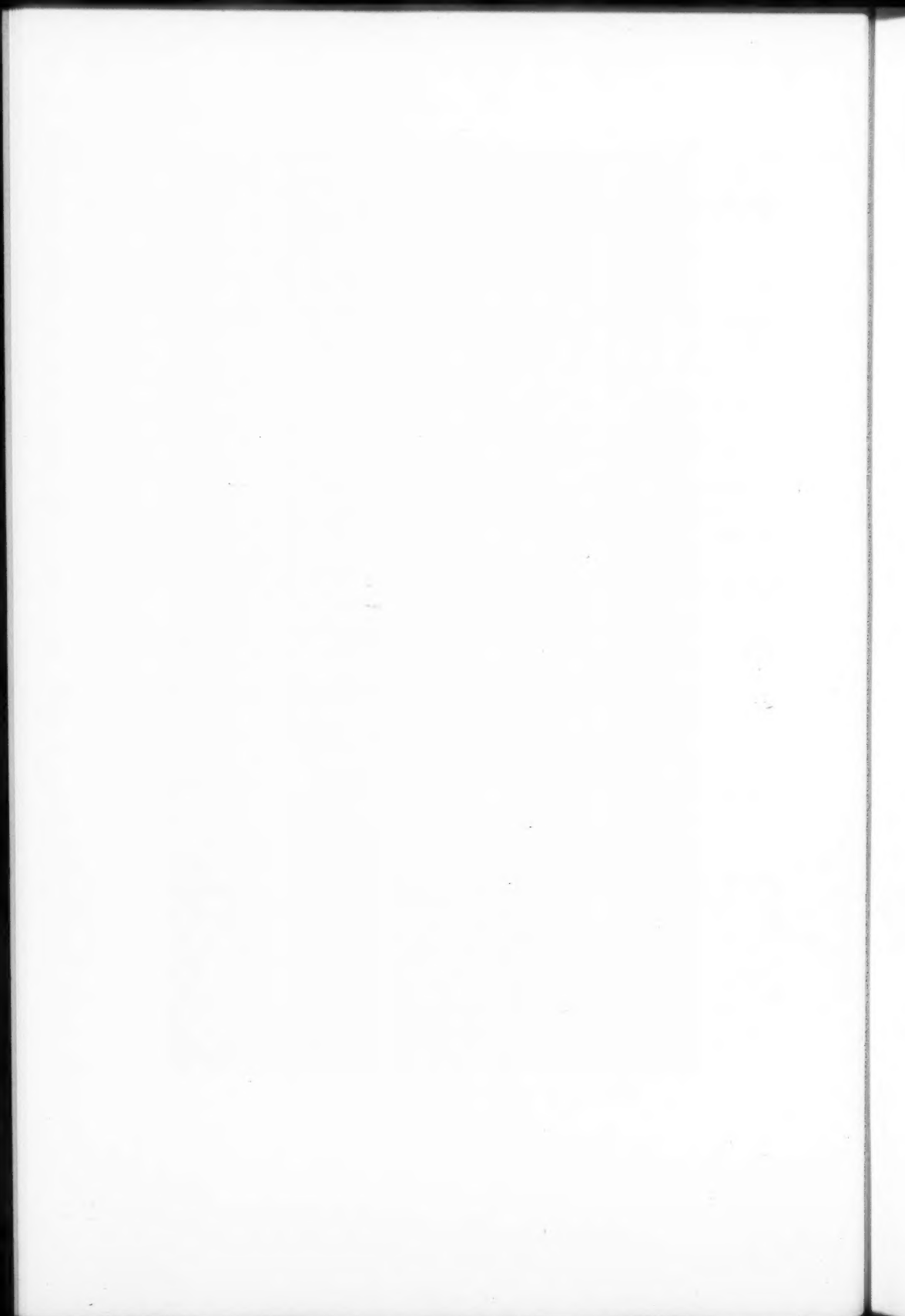
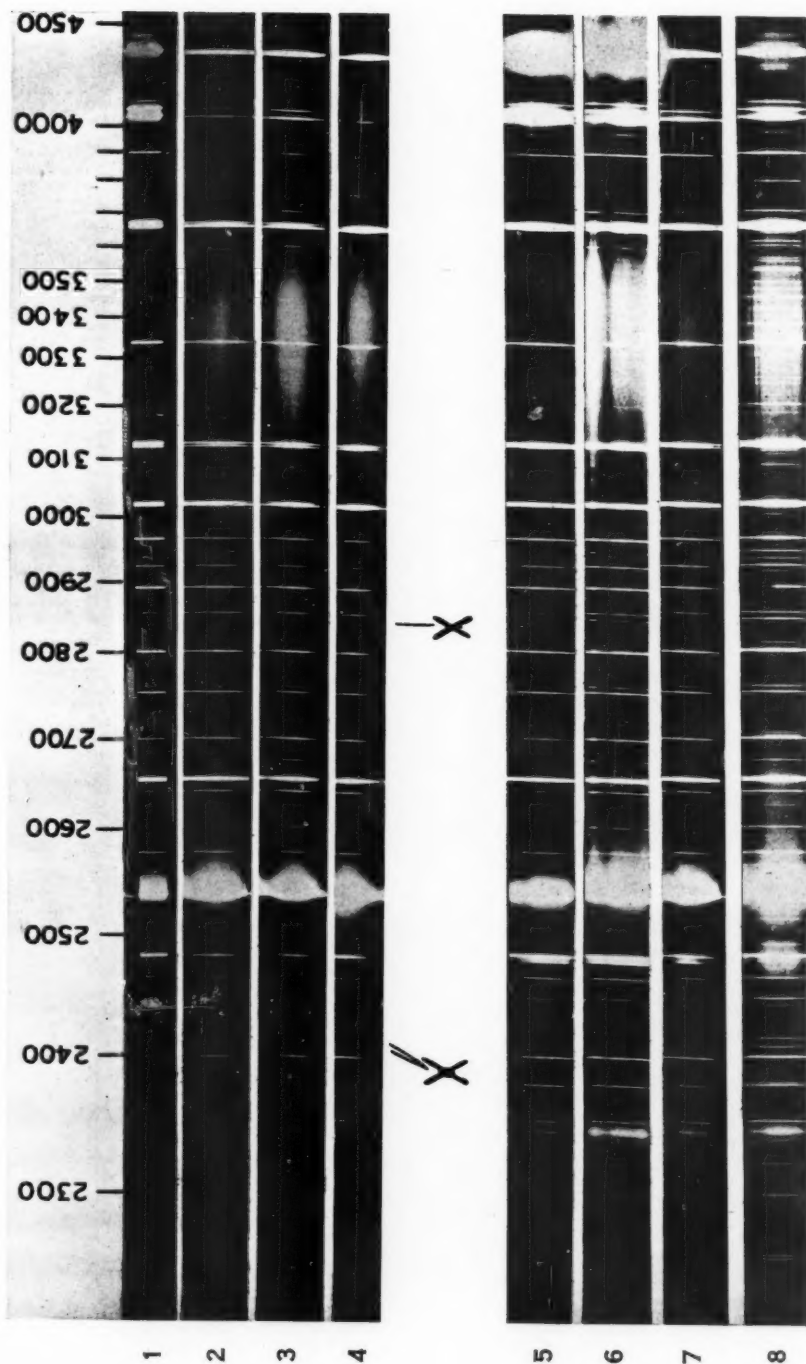


PLATE III



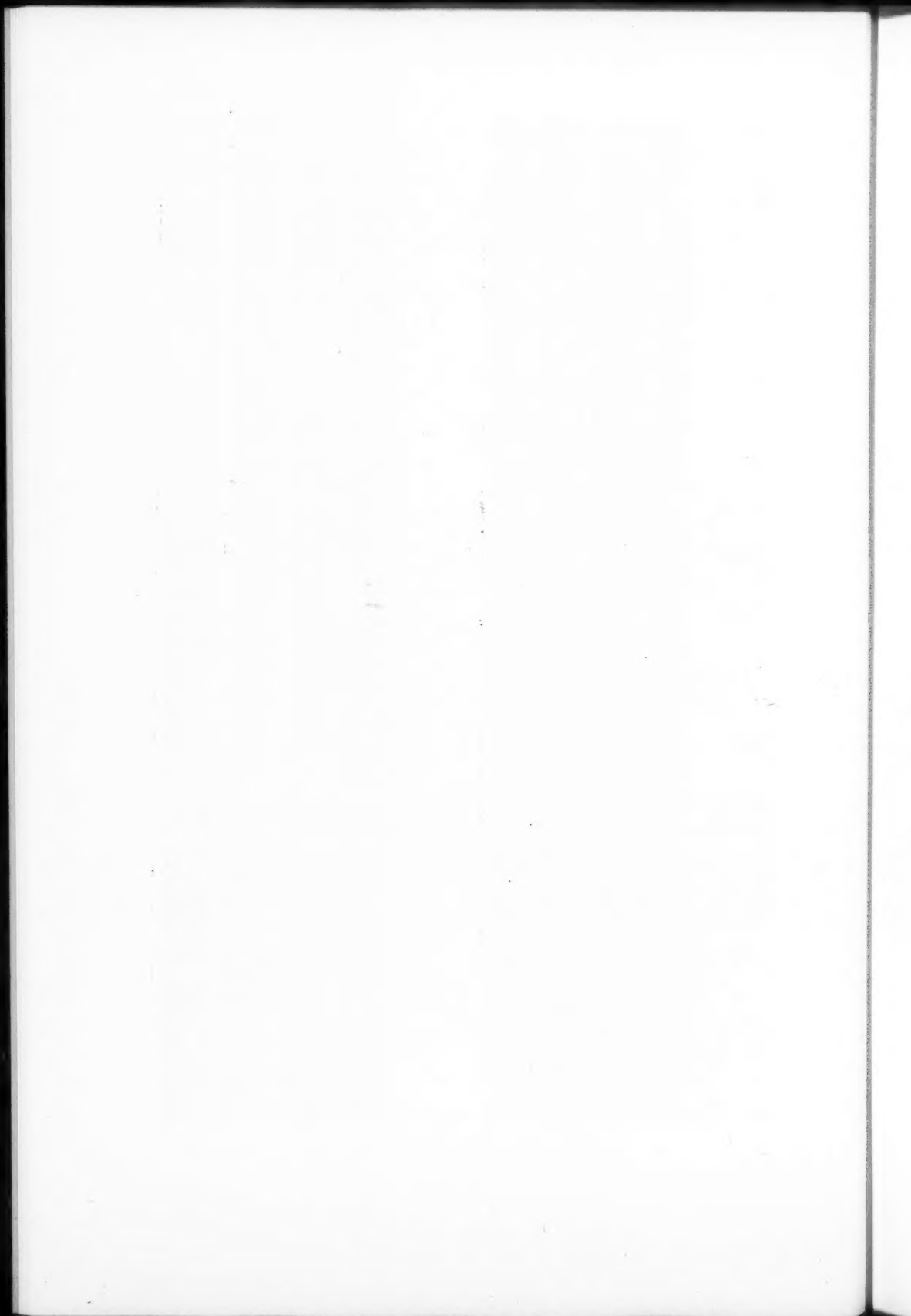
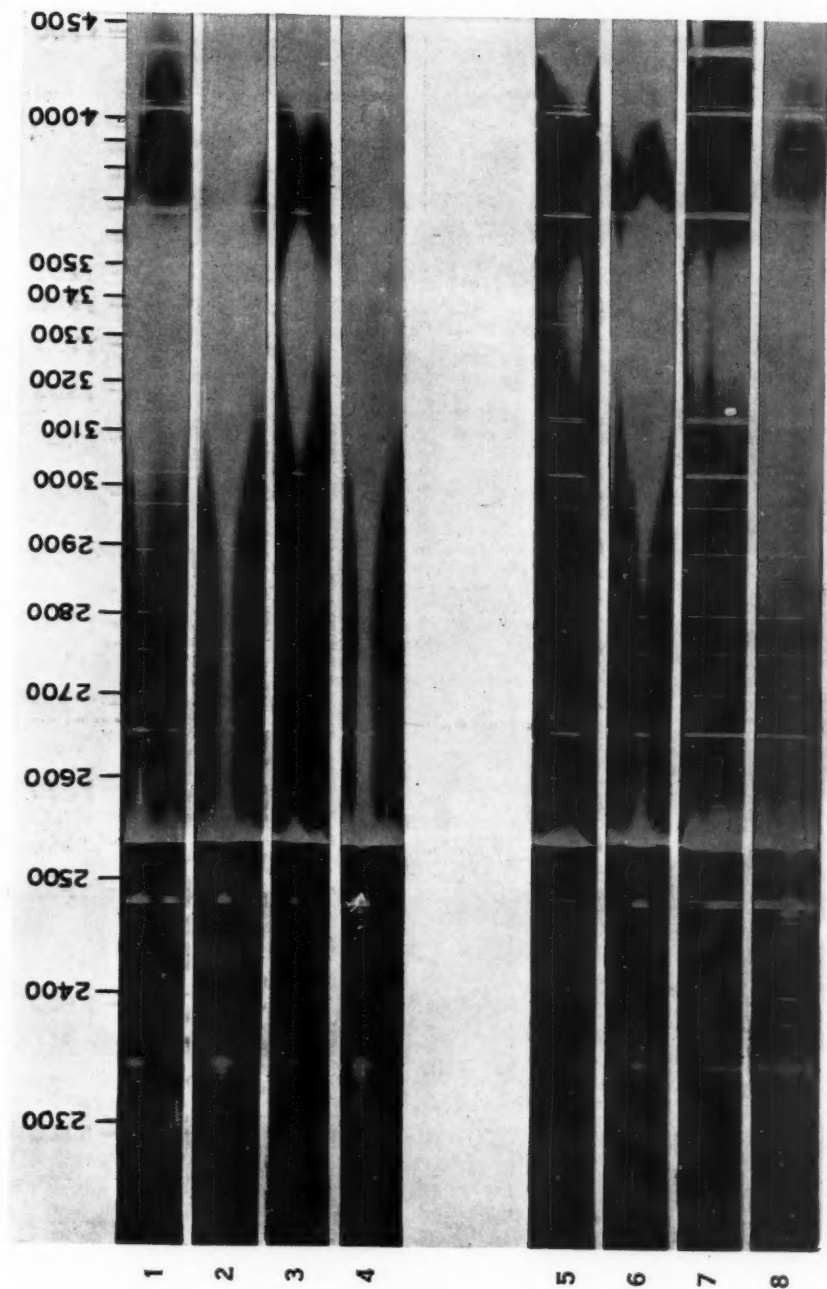
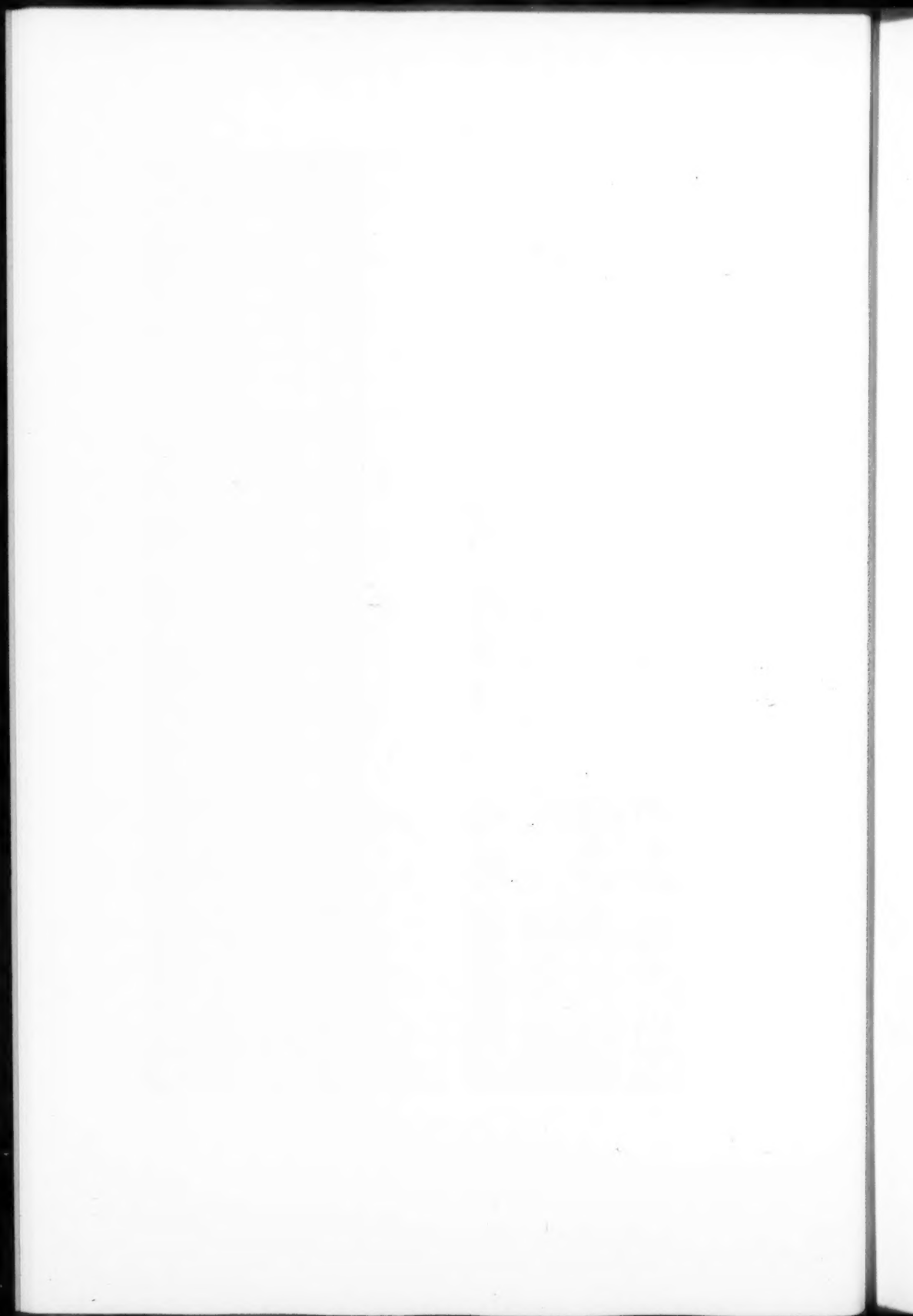


PLATE IV





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THE EFFECT OF ACID MODIFICATION ON SOME PROPERTIES OF STARCH PASTES¹

BY WILFRED GALLAY² AND ADAM C. BELL³

Abstract

Several series of modified potato starches covering a wide range of fluidities were prepared by treatment with dilute hydrochloric acid at 50° C. As in the case of previous results obtained with corn starches, it is shown that the viscosity is dependent on the rate of shear and that the data are well expressed by the exponential relation $F = KP^n$, where F is the flow, P is the pressure, K and n are constants. The value of n decreases rapidly with increasing degree of modification. It is shown that n depends on the volume occupied by the swollen granules in the paste, and that n is much greater in potato starch pastes than in corn starch pastes owing to the greater swelling of the granules. This swelling decreases with increased degree of modification. The stability of the granules in alkaline pastes is described for both potato and corn starches, and the fluidities of alkaline potato pastes are shown to be much greater than those of corn pastes of comparable extent of modification. The gelatinization temperature is shown to rise with increasing modification. At the same time, the power of hydration of the granules decreases and they appear to become denser and more compact. The resistance to mechanical injury becomes greater with increasing modification, and the injured granules swell to a lesser extent. The decreased hydration (hydration plus immobilization) leads to different forms of breakage when the granules are crushed. Prolonged heating of starch pastes causes a rapid decrease in the value of n , owing chiefly to a disruption of the granules with consequent change in the phase-volume ratio.

Viscosity of Potato Starch Pastes

A previous communication dealt with the viscosity of corn starch pastes, measured at varying rates of shear (3). It was shown that there is an exponential relation between flow and pressure, expressed as follows for a torsion viscosimeter:

$$M = KR^{\frac{1}{n}}$$

where M is the deflection of the inner cylinder,

R is the rate of rotation of the outer cylinder,

K and n are constants.

In some instances, there was demonstrated a transition in type of flow at varying pressures and hence a change in the value of the exponent n . Since microscopic examination of a large number of pastes of modified starches showed that the granules had been swollen to varying extent, but not ruptured, it was concluded that the viscosity of comparatively concentrated

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pastes was due chiefly to the volume relations between dispersed phase and dispersion medium, and that a starch paste resembled an emulsion in many respects.

In the present instance, there were prepared several series of acid-modified potato starches, using varying amounts of hydrochloric acid and maintaining other conditions of modification constant. Microscopic examination of a large number of these potato starch pastes showed, as in the case of corn starch, that gelatinization effected a swelling of the granules with no apparent rupture. The swelling was very much greater than that in the case of corn starch, and this might be attributed partly to the larger size of the unswollen granules, since it has been pointed out (1) that the ratio of volume to surface area, and hence swelling pressure per unit area, increases rapidly with increasing size of granules. Observation showed that, with increasing extent of modification of the potato starches, the swelling power of the granule decreased. Hence the volume occupied by a given weight of pasted starch decreased with increasing modification, and the viscosity of the pastes also decreased rapidly.

The viscosities of the pastes were measured at 25° C. in a MacMichael viscosimeter. Figs. 1, 2 and 3 show the flow-pressure relation for three

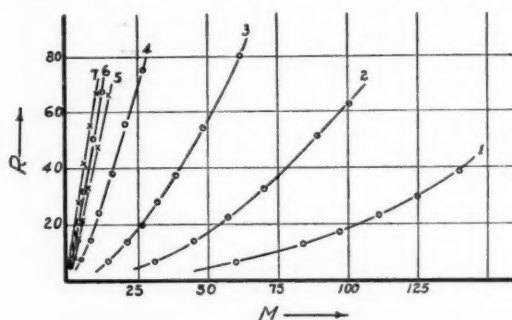


FIG. 1. Flow-pressure relations in 3% potato starch pastes, modified by 1.51% hydrochloric acid for varying periods; numbered in order of increasing degree of modification.

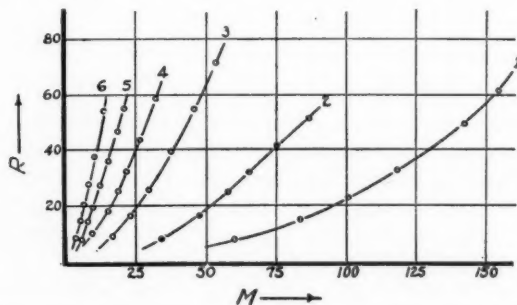


FIG. 2. Flow-pressure relations in 3% potato starch pastes, modified by 2.05% hydrochloric acid for varying periods; numbered in order of increasing degree of modification.

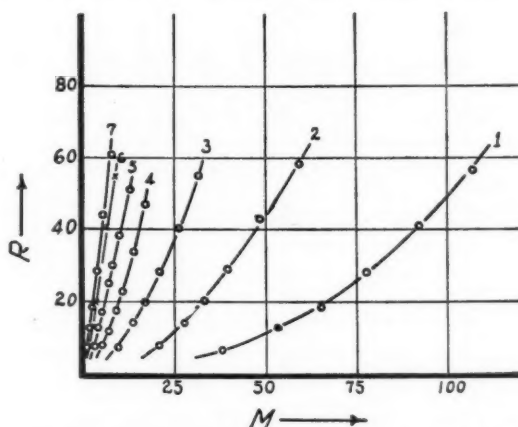


FIG. 3. Flow-pressure relations in 3% potato starch pastes, modified by 2.92% hydrochloric acid for varying periods; numbered in order of increasing degree of modification.

series of acid-modified potato starches in 3% pastes. There is no evidence of any yield value as required by the Schwedoff-Bingham relation, all the curves tending toward the origin. All the curves in each series are convex to the pressure axis, showing an increase in flow greater than linear with respect to increase in driving pressure. In other terms, there is a continual decrease in viscosity with increase in pressure, and hence the exponent n of the exponential relation given above has a value greater than 1 for all these curves.

Figs. 4, 5 and 6 show the flow-pressure relations for these three series on a logarithmic scale. The relations are satisfactorily close to linear as required

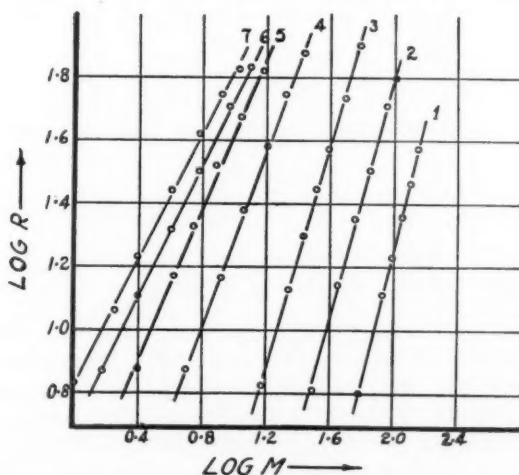


FIG. 4. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 1.

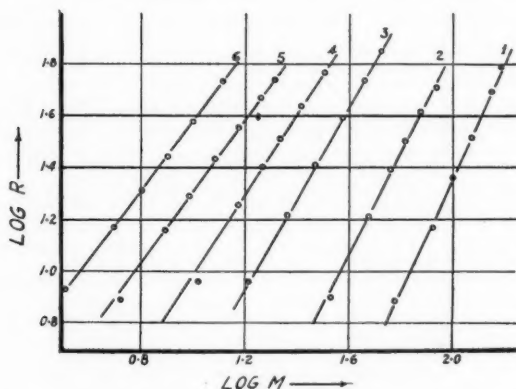


FIG. 5. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 2.

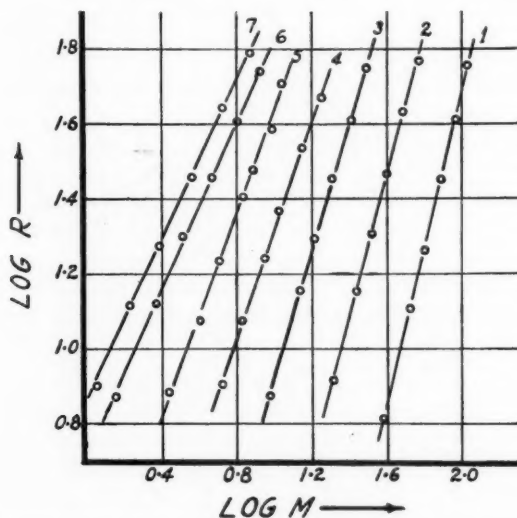


FIG. 6. Flow-pressure relations on a logarithmic scale, from data represented in Fig. 3.

by the exponential relation. The exponent n , represented by the slopes of these lines, is seen to decrease rapidly with increasing extent of modification.

It is noted that there is no evidence of transition from structural to laminar flow in these relations, since the volume relation between the phases at this concentration does not approach that permitting laminar flow even at higher pressures and with the more highly modified starches. Table I is given as representative of a large number of experimental data, showing a comparison between calculated and observed values of M , on the basis of the exponential relation.

TABLE I
VISCOSITIES OF MODIFIED POTATO STARCHES

R	M	
	Obs.	Calc.
a. 1.51% HCl, 50° C., 2 hr.		
Wire No. 26. $M = 25.1R^{1.11}$		
6.3	60.0	60.1
12.9	84.0	84.5
17.1	97.0	96.4
22.9	111.0	110.7
29.2	125.0	124.3
38.5	140.0	138.4
b. 2.05% HCl, 50° C., 2 hr. 40 min.		
Wire No. 26. $M = 2.37R^{1.58}$		
9.2	10.5	9.7
18.3	15.0	14.9
25.6	18.5	18.5
32.6	21.5	21.5
43.7	26.0	26.0
58.8	31.0	31.3
c. 2.92% HCl, 50° C., 1.5 hr.		
Wire No. 26. $M = 2.75R^{1.58}$		
7.5	9.5	9.3
14.3	13.8	13.8
19.7	16.5	16.8
28.3	20.5	20.9
40.5	26.0	25.9
55.0	32.5	31.3

TABLE II
DECREASE IN VALUE OF n AND K WITH ACID-MODIFICATION
($M = KR^{\frac{1}{n}}$)

	Time of modification, min.	n	K
a. 1.51% HCl	120	2.11	25.10
	180	1.86	10.85
	270	1.73	4.79
	390	1.40	1.18
	480	1.23	0.49
	570	1.06	0.23
b. 2.05% HCl	630	1.04	0.16
	40	2.31	26.0
	80	1.90	10.6
	120	1.75	4.62
	160	1.58	2.37
	200	1.38	1.12
c. 2.92% HCl	240	1.34	0.66
	30	2.14	16.21
	60	1.93	6.92
	90	1.65	2.75
	120	1.47	1.29
	150	1.33	0.60
	180	1.15	0.25
	210	1.09	0.17

Table II shows the values of n , obtained graphically, after various periods of modification with different concentrations of hydrochloric acid. The concentrations of the pastes were 3% in all cases, and the temperature of modification, 50° C.

It will be noted from this table that the rate of modification increases markedly with increase in the concentration of acid used. The ratios of time taken to reach a given value of n in the three series is approximately the same for different values of n .

In comparison with corresponding values of n for corn starches previously noted (3), the amount of structure in potato starch pastes of equal concentration is much greater. The great difference in the volume occupied by these pasted starches is strikingly seen in the microscope. A 1% potato starch paste, for example, shows a field crowded with swollen granules, where obviously no laminar flow would be possible. A 1% corn starch paste, on the other hand, shows a field which is not crowded and in which the volume ratio of medium to dispersed phase is relatively high. No direct comparison of rates of modification for the two types of starch can be made, since the swelling powers of the two original unmodified starches show such a great difference. This difference appears, however, to decrease with increased time of modification.

Fluidity of Alkaline Pastes

The commonest method used commercially to determine the fluidity of corn starch pastes is by means of a standard fluidity funnel. The fluidity expresses directly the volume of flow in a given time of a starch pasted at room temperature by the use of 1% sodium hydroxide. Aside from the fact that the rate of shear is not taken into account, the results cannot be directly interpreted since pasting with the aid of alkali produces an effect different from that produced with heat, as far as viscosity is concerned.

Microscopic examination shows in the case of corn and potato starches, both unmodified, that the effect of 1% alkali without heat is to swell the granule strongly without rupture. With slight modification, the results appear very similar, including probably a diminution in the extent to which the granules swell. With somewhat greater modification (corn starch fluidity about 15-20) the granules show partial rupture and the volume occupied by the granular material is greatly decreased. With still further modification, *e.g.*, corn starch fluidity about 35, the granules show total rupture, with a few small segments of granular material less highly hydrated. A similar gradation is observed for potato starch. The alkaline pastes of the unmodified starches therefore possess an internal friction due chiefly to the phase-volume relations as in the aqueous pastes. In slightly modified starches, the viscosity of the alkaline pastes is due partly to this phase-volume relation and partly to the viscosity of the apparently homogeneous solution of a part of the starch in the medium, while with more highly modified starches, the viscosity is due entirely to the latter factor. Following the total rupture

TABLE III
FLUIDITY OF ALKALINE PASTES OF POTATO STARCH

Time of modification, min.	Fluidity		
	a. (1.51% HCl)	b. (2.05% HCl)	c. (2.92% HCl)
30			6.0
40		3.0	
60			14.0
80		8.0	
90			22.5
120	5.5	15.5	37.0
150			53.0
160		25.0	
180	12.0		64.0
200		37.0	
210			73.0
240		52.8	
270	19.2		
390	38.5		
480	53.0		
570	66.0		
630	74.0		

of the granule, the viscosity of the alkaline paste is still further reduced with increased modification. Whether this is due to a decreased solvation or to a further phase-volume decrease will be further discussed elsewhere (2).

The fluidities of alkaline pastes of the modified potato starches prepared were measured in the same way as that generally employed for corn starches. Table III shows the results obtained.

These fluidities form an interesting comparison with fluidities of modified corn starches in alkaline pastes. In the case of aqueous pastes, the exponent

n is probably a function of the phase-volume relation in the heterogeneous system, whereas in the alkaline pastes, the system is at first heterogeneous, changing to a colloidal solution at relatively low fluidities. Fig. 7 shows

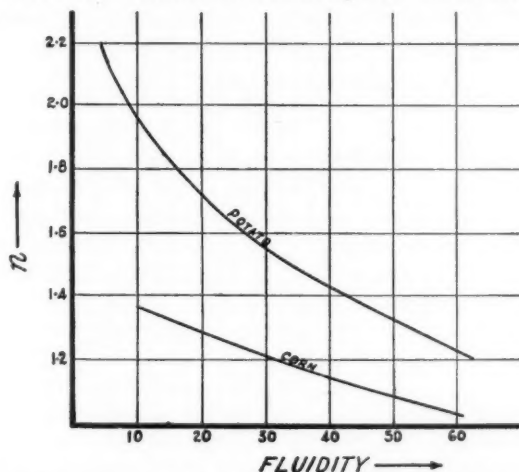


FIG. 7. Relation between n of 3% aqueous pastes and fluidity of 5% alkaline pastes. Data averaged from three series of acid-modified potato starches and two series of acid-modified corn starches.

the relation between n (aqueous) in 3% paste and fluidity (alkaline) in 5% concentration. Each curve is the average of several measurements. It is noted that for the same value of n , the fluidities of the potato starches are much higher than those of corn starch. This is apparently not true of the unruptured granules, since unmodified and only very slightly modified potato starches show lower fluidities than the corresponding corn starches. This is apparently connected with the effect of sodium hydroxide on the phosphate radicle of the potato starch.

Swelling Power and Elasticity of the Granules

When starch is suspended in cold water, a definite small swelling of the granules takes place (1). As the temperature of the suspension is raised, this swelling is slowly increased. Subsequently, within a small range of increase in temperature, this swelling increases enormously. This phenomenon is commonly termed the gelatinization of a starch, and the corresponding temperature is termed the gelatinization point. The latter varies quite widely for each type of starch, and within narrower limits also for different samples of the same type of starch. It is apparent that there is a gelatinization range rather than a gelatinization point. Furthermore, with increase in temperature, there is a further swelling, so that the so-called gelatinization is not complete within the gelatinization range (1).

When a series of acid-modified starches is considered, the major effect of modification is a decreased swelling of the granules under the same conditions

of gelatinization (3). This may be ascribed to either or both of the following factors: (i) a decrease in the ability of the contents of the granule to swell, (ii) a change in the nature of the material constituting the outer portion of the granule, leading to greater rigidity of the granule. Table IV shows the

TABLE IV
GELATINIZATION OF ACID-MODIFIED STARCHES

Starches in order of increasing degree of modification	Gelatinization temp., °C.
Unmodified	63
1	65
2	67.5
3	68.5
4	69.8
5	69.8
6	70.5
7	71.5

"gelatinization temperatures" for a series of acid-modified potato starches. Each figure is the average of several determinations, the temperature being that at which a fairly sharp increase in viscosity and change in the appearance of the suspension was noted.

It is evident that an increased temperature is necessary to bring about this sharp increase in swelling, with increased degree of modifica-

tion. With increase of the latter, the starch granules have suffered a loss in the power of hydration of their contents, where hydration includes actual bound solvent and immobilized solvent.

An excellent picture of these changes is obtained by dry-grinding starches of varying degrees of modification. Samples of each starch were ground under the same conditions in a ball mill and samples withdrawn at regular intervals. Microscopic examination was made of these samples after suspension in water for several hours at room temperature. As was to be expected, the grinding resulted in a partial cracking of the granules. It was found, however, that the resistance to cracking was greater with increasing degree of modification of the starch. Furthermore, whereas in the unmodified starch the swelling of the cracked granules was very great, there was found to be a continual decrease in this swelling with increasing degree of modification of the starch.

Table V shows a summary of the results obtained in the measurement of the extent of swelling of these ground starches. The measurements were

TABLE V
SWELLING OF GROUND STARCHES

Starch	Vol. (cc.) occupied by 5 gm. after grinding for			
	3 hr.	8 hr.	24 hr.	48 hr.
Potato unmodified	18	43	83	110
Potato modified 1	15	24	48	65
Potato modified 2	16	24	42	49
Potato modified 3	15	22.5	37	42
Potato modified 4	13	20	27	33
Potato modified 5	13.5	19	24	28
Potato modified 6	13	18	23	25
Potato modified 7	11	15.5	22.5	27
Corn unmodified	10	12.5	20.5	30.5

made after five hours' suspension of the starch sample (5 gm.) in water at room temperature. Included with this series of potato starches also was a sample of unmodified corn starch. The numbers are in ascending order of extent of modification.

On crushing specimens of these starches under cover glasses on microscope slides, it was found that there was a regular gradation from irregular cracking, with the original form more or less preserved in the case of unmodified starch, to a breakage into compact wedge-shaped pieces in the case of a highly modified starch. The impression obtained was that of a gradually decreasing plasticity of the granule, the unmodified granule crushing like a swollen particle, the highly modified starch crushing to segments like a rigid body. The greater "brittleness" of a modified granule has been noted elsewhere (4).

Generally speaking, it would appear that the power of hydration decreases with increased modification. This leads to a greater resistance to mechanical impact and to a different form of splitting when the granule is mechanically broken. Decreased hydration appears to lead to a denser and more compact structure with results as noted above.

The hypothesis has been advanced by various authors that the effect of acid modification is due to a decrease in the phosphoric acid content of the starch. In the present instance this analysis was carried out on a range of modified starches. It was found that the variations in phosphorus pentoxide content were within the limits of experimental error. It would appear rather that the primary effect is one of depolymerization of a high molecular weight polymer.

Decrease in Viscosity of Pastes with Continued Heating

The change in viscosity with prolonged heating is important commercially, as in the case of the sizing of yarn. Pastes of potato starches of varying degrees of modification were maintained at 97–98° C. under reflux, and samples were withdrawn at regular intervals for examination and viscosity determination. No additional agitation was used. The pastes were all in 3% concentration.

It was found that there was a gradual increase in the percentage of ruptured granules with increased time of heating. The exponent n of the exponential relation was found to decrease sharply, *e.g.*, in the case of unmodified potato starch the decrease in the value of n was found to be from about 2.80 for the original starch to 1.09 after seven hours of heating. Unfortunately, at the concentration chosen, most of the heated pastes showed apparent turbulence in the viscosimeter. Table VI shows some results obtained where n is greater than 1.

TABLE VI
EFFECT OF HEATING AT 97° C. ON THE VALUE OF n

Time of heating, hr.	n (3% conc.)		
	Unmodified potato	Modified 1	Modified 2
Fresh	2.80	1.95	1.34
1	1.96	1.70	1.10
2	1.71	1.34	1.03
4	1.30	1.05	
6	1.15	1.04	
7	1.09		

With continued heating, there is a decrease in the volume occupied by the starch granules. The viscosity of the medium increases owing to the dissolved starch, but the net effect is one of a large decrease in the viscosity of the system.

Experimental

The preparation of aqueous starch pastes, alkaline pastes and solutions, and viscosity and fluidity determinations were carried out as described elsewhere (3).

For determination of the gelatinization temperature, a 2% suspension of starch was immersed in a boiling water bath, the heating arrangement removed from the latter and the starch suspension stirred slowly at a standard rate, until a sharp change was noted in the viscosity and appearance of the suspension.

The effect of dry-grinding was noted as follows: 100 gm. of each starch was placed in a quart ball mill with a standard weight of pebbles, and the ball mill rotated at constant speed. Representative samples (15 gm.) were withdrawn at the time intervals noted. For determinations of swelling capacity, 5 gm. of each sample was suspended in 90 cc. of distilled water and the suspension left undisturbed for five hours after which the volume of suspended starch was read.

For the effect of continued heating on the viscosity of pastes, 800 cc. of 3% paste was prepared by pouring a concentrated suspension into boiling water. The paste was then transferred to a boiling water bath and maintained at 97-98° C. under reflux. Samples (100 cc.) were withdrawn after the time intervals noted. Viscosity measurements were made at 25° C. in a MacMichael viscosimeter as described above.

References

1. ALSBERG, C. L. *Ind. Eng. Chem.* 18 : 190-193. 1926.
2. GALLAY, W. *Can. J. Research, B*, 14: 391-403. 1936.
3. GALLAY, W. and BELL, A. C. *Can. J. Research, B*, 14 : 360-372. 1936.
4. SJOSTROM, O. A. *Ind. Eng. Chem.* 28 : 63-74. 1936.

THE EFFECT OF CONCENTRATION ON THE VISCOSITY OF STARCH PASTES AND OF LYOPHILIC SOLS¹

BY WILFRED GALLAY²

Abstract

The critical concentration of a starch paste is the limiting concentration above which structural flow is apparent. The inverse of the critical concentration, termed the effective volume, is the minimum volume of solution per gram of starch below which structural flow is apparent. The critical concentrations and effective volumes have been measured for series of pastes of acid-modified corn and potato starches, and the effective volume has been shown to decrease with increasing degree of modification. The specific viscosities per unit concentration of these pastes, at concentrations below the critical, increases linearly with the effective volume, and the proportionality constants found are compared with those derived from the equations of Einstein and of Hatschek. The effects of phase-volume ratio and ease of deformation of the dispersed phase on the viscosity of a system are discussed, and previous relations applied to experimental data obtained in the present instance. Residual structure below the critical concentration is discussed. Above the critical concentration, the viscosity is dependent on the rate of shear, and the equation $F = KP^n$ expresses the experimental data well, where F is the flow, P is the pressure, K and n are constants. For two starches investigated, within the range of concentrations used n has been found to increase linearly with the concentration c , dn/dc being dependent on the elasticity or deformability of the granules.

The form of lyophilic colloids in solution is discussed and agreement is expressed with the conception of Haller that the long-chain molecules, owing primarily to the free rotatability of the valence linkages, are irregularly bent and tangled in solution, as opposed to Staudinger's conception of straight rigid chains. These molecules occupy on the average a form approximating to the spherical, and solvation is due chiefly to immobilization. A dextrin in solution was found to have a $\left(\frac{\eta_{sp}}{c} \div \text{effective volume}\right)$ ratio close to that of a pasted starch, and the forms of the two are probably similar. A lyophilic sol is considered heterogeneous and similar in many respects to an emulsion, with a very highly deformable discontinuous phase. The viscosity of such a system is due to phase-volume relations, modified by the ease of deformation of the dispersed phase, and the particular characteristics of these important sols admit of explanation on this basis.

The Transition from Laminar to Structural Flow in Starch Pastes

The viscosity of a starch paste at higher concentrations is dependent on the rate of shear, and the flow-pressure relation is satisfactorily represented in most cases (7, 8) by

$$F = KP^n,$$

where F is the speed of flow,

P is the pressure,

K and n are constants.

In true solutions, n is equal to 1 and the flow is laminar. In starch pastes, however, at higher concentrations n is greater than 1 and the viscosity decreases with increasing pressure. In these systems, the speed of flow is linearly proportional to a higher power of the pressure, this power being calculable from the $\log F / \log P$ graph. This type of flow has been termed

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structural flow (Ostwald) and since it has been shown (8) that the viscosity of a starch paste depends largely on the volume occupied by the swollen granules, it is apparent that there must be a deformation or orientation of these granules with increase in pressure, leading to a decrease in viscosity.

If the concentration of the paste is decreased, there is a decrease in the phase-volume ratio with a consequent decrease in the exponent n representing the structure. It has been shown in a previous communication (7) that in systems with only a little structure, there may be a transition from structural to laminar flow with increase in pressure. Obviously the concentration can be reduced to a value just below that at which structure is measurable with the apparatus used. Such a concentration may be termed the critical concentration of the system, or the concentration at which there is a transition from laminar to structural flow. Above the critical concentration, the total volume available is insufficient for free movement of the swollen granules when sheared, and the reciprocal of the critical concentration (in gm. per cc.) may be regarded therefore as the total volume affected by 1 gm. of starch in the paste. This is obviously greater than the actual volume of the dispersed phase, but no regular correction can be applied for voids since the type of packing varies with the type of starch, the degree of modification of the starch, etc. Furthermore, the swollen granules vary greatly in size and somewhat in shape and hence the packing is quite irregular. However, the total volume influenced or the "effective volume" appears to be reasonably constant for the same starch in the same concentration.

The Viscosity of Starch Pastes below the Critical Concentration

The following expression has been deduced by Einstein (2, 3) for the case of an ideal suspension:

$$\eta' = \eta(1 + 2.5\phi),$$

where η' is the viscosity of the suspension, η is the viscosity of the dispersion medium, and ϕ is the ratio of aggregate volume of dispersed phase to the volume of the suspension. In the analytical treatment, the suspended particles are assumed to be rigid spheres having a diameter small in comparison with the distance between the spheres but large compared with the dimensions of the molecules of the dispersion medium. Since the diameter of the particles of dispersed phase does not occur in the expression, the viscosity of a suspension should increase linearly with the volume of the dispersed phase and independently of the degree of dispersion.

The above expression may be written

$$\eta' = \eta \left(1 + 2.5 \frac{fc}{100} \right),$$

where f is the volume in cc. occupied by 1 gm. of suspension and c is the concentration of the suspension in gm. per 100 cc.

$$\text{or } \eta_{sp} = 2.5 \frac{fc}{100},$$

where η_{sp} is the specific viscosity of the suspension, i.e. the viscosity of the

suspension relative to the dispersion medium, minus unity. η_{sp} denotes the added viscosity due to the presence of the suspended particles, and therefore the added viscosity due to the presence of 1 gm. of dispersed phase should be linearly proportional to the volume in cc. occupied by 1 gm. of suspended particles, *i.e.*

$$\frac{\eta_{sp}}{c} = Kf, \quad (1)$$

where K , according to the equation of Einstein, has a value of 0.025.

A number of attempts at verification of the linear equation have been made with varying results (5, p. 368). Many of the tests have been made on lyophilic colloids and no method has been found hitherto of measuring the effective volume of the dispersed phase. Furthermore, as has been pointed out by Hatschek (14, pp. 738-750), many of the measurements have been made in the region where the viscosity is dependent on the rate of shear. In some instances (5), linear relations have been obtained with widely varying constants of proportionality.

In the present instance, there were available a large range of acid-modified potato and corn starches, whose properties have been described elsewhere (7, 8). It has been shown that the viscosity of their pastes decreases with increasing degree of modification, owing to a continuous reduction in swelling power of the granules and hence to a decreased volume occupied by the suspended particles.

The procedure used in the determination of each critical concentration was as follows: The viscosity of pastes of varying concentration over a wide range of shear was measured in a torsional viscosimeter. The critical concentration was chosen as the highest concentration at which the flow was still laminar, *i.e.*, where the flow is linearly proportional to the pressure. Fig. 1 shows the increase in critical concentration in acid-modified corn

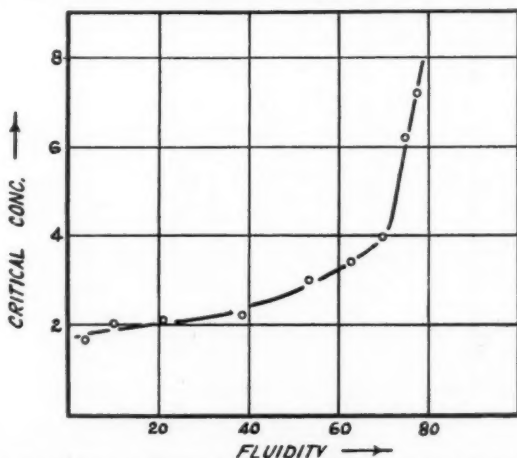


FIG. 1. Relation between critical concentration and fluidity in acid-modified corn starches.

starches with increasing degree of modification, the commercially adopted "fluidity" of a 5% alkaline paste being used to characterize the extent of modification. A similar increase was obtained in the case of potato starch.

The viscosities of pastes of these starches were then measured at concentrations close to but below the critical. Even by employing a rigidly standard procedure in the preparation of the pastes and in the viscosity measurements, it was found that the variation in viscosity results was quite appreciable and, therefore, in most instances, the mean of several determinations was taken. Because of the nature of the material, with irregular swelling, variations in sizes of particles and irregular packing, no great accuracy is claimed for these determinations, but the trend of relations is quite clear.

Figs. 2 and 3 show the relation between specific viscosity per unit concentration and the effective volume for series of corn starches and potato starches respectively. The results show an approximate linear relation in both cases, there being no indication of a sharp increase in viscosity for greater effective volume. The calculated proportionality factors (from the graphs) are as follows:

$$\text{Corn starch} \quad \frac{\eta_{sp}}{c} = 0.059 V \text{ or } \eta' = \eta(1 + 5.9 V)$$

$$\text{Potato starch} \quad \frac{\eta_{sp}}{c} = 0.089 V \text{ or } \eta' = \eta(1 + 8.9 V)$$

where V is the effective volume influenced by 1 gm. of dispersed phase. V is a function of f , depending on several factors of which the most important is probably the shape of the particles. The greater the aberration from the spherical in shape, the greater will be the ratio V/f .

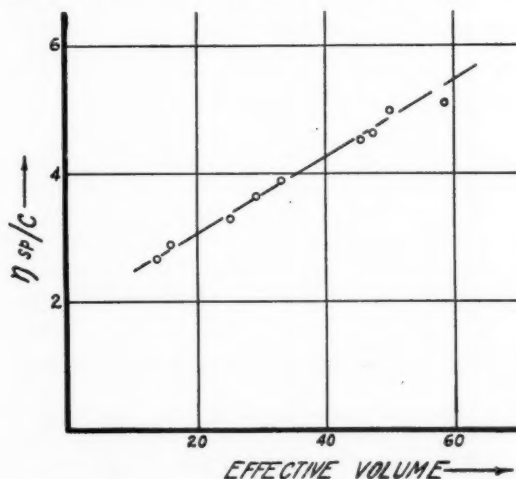


FIG. 2. Increase in specific viscosity per unit concentration with increase in "effective volume" in acid-modified corn starches.

Based on the premises that the particles of the dispersed phase obey Stoke's law, that they do not come in contact with one another and that sufficient liquid cross section remains so that the mobility of the continuous phase is not reduced, Hatschek (11) has derived the following relation between viscosity and volume of dispersed phase in dilute suspensions or emulsions:

$$\eta' = \eta(1 + 4.5f) .$$

This expression differs from that of Einstein in the proportionality factor. In a study of the viscosity of blood from various sources, Trevan (24) determined f by centrifuging, and found that the following relation held up to about 45% concentration by volume:

$$\eta' = \eta(1 + 6.3f) .$$

It is interesting to note the comparison between this relation and those obtained in the present instance, since the heterogeneous systems blood and starch pastes show many characteristics in common.

An approximate measure of the actual volumes occupied by the swollen granules was obtained in the present instance, as follows: Unmodified potato and corn starches at their respective critical concentrations were gelatinized under the same conditions as those used generally in this work (7, 8), and then aliquot portions of the pastes cooled to 25° C. were centrifuged at about 2,000 r.p.m. Centrifuging was continued until the volume of the separated granules reached a minimum. The percentages by volume were 31.5 and

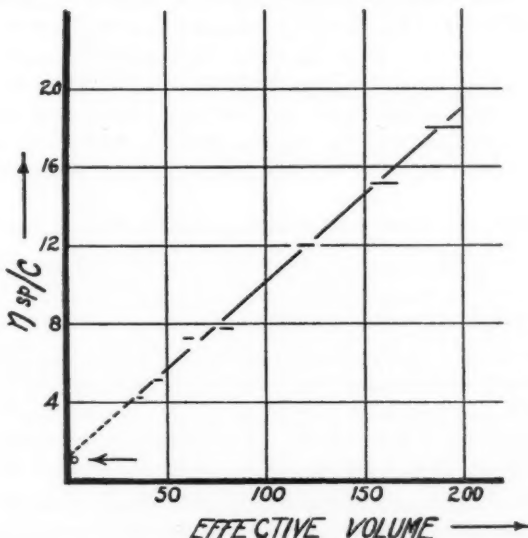


FIG. 3. Increase in specific viscosity per unit concentration with increase in "effective volume" in acid-modified potato starches. The circle represents the same relation for a highly converted dextrin. The bars show range of effective volumes, as calculated from upper and lower values for the corresponding critical concentrations.

35.3 for corn and potato starches respectively. If then, the effective volumes determined are corrected by these figures, the proportionality factors become 1.86 and 3.14 for corn and potato starches respectively, averaging 2.5. Harrison (10) obtained the factor 4.75 for unmodified starches of different types, by pasting the starches in 1% concentration at a temperature just above the gelatinization range, and measuring the volume by centrifuging. With gelatinization at a higher temperature, the swelling is increased and consequently this factor of 4.75 would be greatly reduced.

Another important factor is the residual structure below the critical concentration. It appears very probable that even at lower concentrations the phase-volume ratio is sufficiently high to afford an increment of the internal friction due to some interaction of the particles of the dispersed phase. This will add to the specific viscosity and raise the value of the proportionality factor between η_{sp} and V . This residual structure will obviously be greater with greater departure from the spherical in particle shape, and will vary also with the deformability or elasticity of the suspended particles. Potato starch granules, when pasted, vary more from the spherical than pasted corn starch granules, and also show greater deformability, and it is to be expected therefore that the proportionality factor between η_{sp} and V is somewhat greater for potato starch than for corn starch.

The effect of rate of shear on the viscosity of lyophilic sols and similar systems at concentrations below the critical has been discussed at length by Ostwald (16). In a number of instances it has been shown that the critical Reynolds number is actually much smaller for a lyophilic sol than for the dispersion medium alone. In some cases there appears to be laminar flow only over a very short range of pressure, the structural flow at low rates of shear changing almost directly to turbulent flow at higher rates of shear. In the present instance, calculations of viscosity were made only on data showing laminar flow, in order to avoid the anomalous effects of turbulence.

The Viscosity of Starch Pastes above the Critical Concentration

The viscosity of starch pastes, as in the case of lyophilic sols, increases very steeply at higher concentrations. This is well shown in Fig. 4, reproduced from data of Farrow and Lowe (4).

Although the curves show no discontinuities, these authors have noted changes in the viscosity-concentration curves at about 0.7% and 1.5% for potato and corn starches, respectively, at 90°C. In the present work, the critical concentrations of potato and corn starches have been found to be approximately 0.45% and 1.8% at 25°C.

Above the critical concentration, the viscosity is dependent on the rate of shear. Since the latter is in turn partly dependent on the dimensions of the viscosimeter used, the viscosity of a concentrated starch paste will vary with the instrument used. This is true particularly of the ordinary type of efflux viscosimeter where no account is taken of the shear, and where the shear

varies in a complicated way during flow. This effect of shear is well shown in Fig. 4, where the relative viscosity of two pastes as measured in instruments of different dimensions is plotted against concentration.

A number of empirical equations have been proposed relating viscosity and concentration in lyophilic sols. These have been summarized elsewhere (17, 18). The one that has received most attention is that of Arrhenius (1):

$$\log \eta_r = Kc$$

$$\text{or, } \eta_r = 10^{Kc}$$

where η_r is the relative viscosity, c is the concentration and K is a constant. Since the relative viscosity depends on the rate of shear, K cannot be a constant for apparatus of varying dimensions and for different driving pressures.

The problem of the viscosity of a heterogeneous system containing two easily deformable phases has been treated synthetically by Hatschek (12). The percentage of dispersed phase is assumed to be so high that the droplets assume polyhedral shape. If the system is sheared, the polyhedra are deformed, and it is assumed that the whole of the shear takes place in the layers of continuous phase parallel to the plane of shearing. The relation derived is as follows:

$$\eta' = \frac{\eta}{1 - \sqrt[3]{f}} \quad (2)$$

Hess (15) has given a synthetic treatment, somewhat similar in principle to that of Hatschek, of the problem of suspensions of rigid spheres. An ideal arrangement of the spheres has been assumed, leaving the whole of the liquid cross section available for the flow, excepting regions of unmobilized liquid surrounding the particles. The following relation was derived:

$$\eta' = \frac{\eta}{1 - af} \quad (3)$$

where af is the "functional volume" of the dispersed phase. The value of a is always greater than 1 and was found to vary from 1.16 to 2.50 in suspensions of blood corpuscles, depending on the concentration. Hatschek has noted (13) that Equations (2) and (3) are identical if $a = 1/\sqrt[3]{f^2}$, and he has shown that this condition is satisfied almost exactly by the suspensions of red blood corpuscles investigated by Hess (15). However, the viscosity of such a system is undoubtedly dependent on the rate of shear, and the effect of this

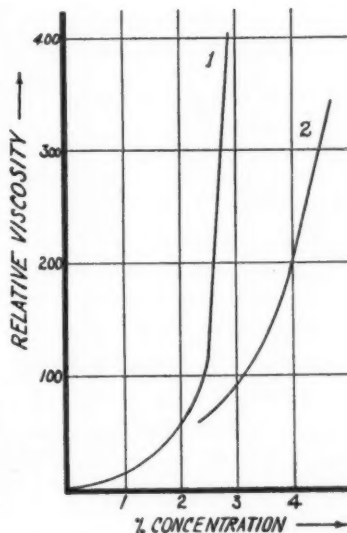


FIG. 4. The increase in relative viscosity with concentration in potato starch pastes (Farrow and Lowe, 1923). Measurements made in two Ostwald viscometers, 1 and 2, of different dimensions, showing the important effect of rate of shear.

on the results obtained in the verification of these relations is very difficult to determine. Testing Equation (2) in the case of paraffin emulsions, Sibree (19, 20) has shown that $\frac{\phi_{\text{calc.}}}{\phi_{\text{meas.}}}$ is equal to 1.3 for concentrations over 60%.

He concluded therefore that the active volume of the disperse phase is 30% greater than that of the paraffin itself, and that the dispersion liquid is "hydrodynamically" affected for a considerable distance from the interface.

Since the suspensions examined by Hess included some of concentrations far lower than those considered theoretically by Hatschek, it is interesting to note the values of f calculated from data in the present instance, using the relation of Hatschek. Equation (2) may be written in the following form:

$$f = \left(\frac{\eta_{sp}}{\eta_r} \right)^3 \quad (4)$$

Since f is the ratio of volume of dispersed phase to the total volume of the suspension, f/c is the volume occupied by 1 gm. of starch together with associated solvent. Table I shows a comparison between the calculated

TABLE I
EFFECTIVE VOLUMES OF DISPERSED PHASE IN CORN STARCH PASTES

No.	$\frac{f}{c} = \left(\frac{\eta_{sp}}{\eta_r} \right)^3 \cdot \frac{1}{c}$, cc.	Critical concentration, %	V , cc.	$\frac{f/c}{V}$, % (average)
1	44.6	1.6-1.7	58.8-62.5	73.6
2	39.6	2.0	50.0	79.2
3	35.7	2.1	47.6	75.0
4	35.6	2.2	45.4	78.4
5	26.4	3.0	33.3	79.2
6	23.9	3.4	29.4	81.3
7	20.8	3.9-4.0	25.0-25.6	82.2
8	13.7	6.2	16.1	85.1
9	11.9	7.2	13.9	85.6

values of f/c and the corresponding V obtained directly from the critical concentrations measured for a series of acid-modified corn starches. The starches are numbered in order of increasing degree of modification (decreased swelling power in pastes). The values of f/c are averages of several determinations.

Table II shows similar results for a series of acid-modified potato starches, numbered in order of increasing degree of modification.

It is seen that f/c has a value about 80% that of V in each series. Since V is derived on the assumption that the whole of the available volume is influenced or affected (but not occupied) at the critical concentration, it is to be expected that V should be consistently greater than f/c . It is interesting to note that values of the same order are obtained by these two methods.

TABLE II
EFFECTIVE VOLUMES OF DISPERSED PHASE IN POTATO STARCH PASTES

No.	$\frac{f}{c} = \left(\frac{\eta_{sp}}{\eta_r}\right)^{\frac{1}{n}} \cdot \frac{1}{c}$, cc.	Critical concentration, %	V , cc.	$\frac{f/c}{V}$, % (average)
1	156	0.5-0.55	182-200	81.9
2	126	0.6-0.65	154-167	78.6
3	93.0	0.8-0.85	118-125	76.6
4	63.3	1.2-1.3	76.9-83.3	79.2
5	48.8	1.6-1.7	58.8-62.5	80.6
6	37.2	2.1-2.2	45.4-47.6	80.0
7	30.0	2.7	37.0	81.0

In the foregoing there has been considered viscosity-concentration relations chiefly from the point of view of the volume occupied in pastes by starches of different degrees of modification. If the viscosity-concentration relation in pastes of the same starch is determined at concentrations above the critical, the structure in the paste is an important factor, since $F = KP^n$ and a modified law of flow must be used, *viz.*

$$\eta = K \frac{P^n}{F}, \quad (5)$$

where K is a constant of the viscosimeter used. In order to determine the variation of the exponent n with concentration, viscosity determinations of series of unmodified potato and corn starches were made in a MacMichael viscosimeter. The value for n was obtained graphically as the slope in the logarithmic plot of $M = KR^{\frac{1}{n}}$, where M is the deflection of the torsion wire in degrees MacMichael, R is the rate of rotation of the outer cylinder in revolutions per minute, n and K are constants.

Table III shows the variation in n with concentration of paste.

TABLE III
INCREASE IN n WITH CONCENTRATION

Starch	Concentration, %	n
Corn	2	1.10
	3	2.14
	4	3.19
	5	4.46
	6	5.40
Potato	0.55	1.04
	0.7	1.24
	1.0	1.28
	1.5	1.80
	2.0	2.04
	2.5	2.44

Fig. 5 shows this relation for the two starches. Within the range of concentration investigated, there is a linear increase in n with increasing concentration. Extrapolation to value of 1.0 for n (laminar flow) gives concentrations of 0.45% and 1.9% for potato and corn starches respectively. The critical concentration, above which structure was found, was determined to be 0.45% and 1.8% respectively. The ease of deformation of the pasted potato starch granules has been noted above as being greater than that of corn starch, and it is to be expected that n should increase more rapidly with increasing concentration in the case of corn starch.

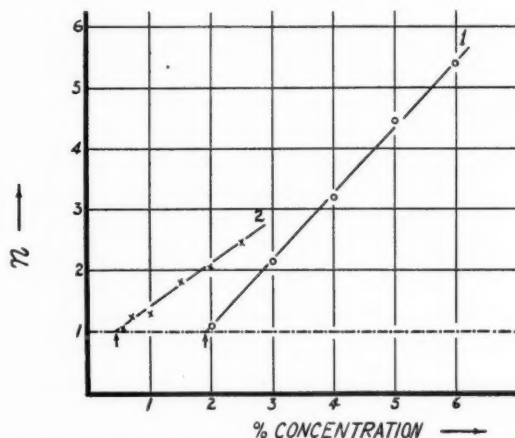


FIG. 5. Increase in η with concentration in pastes of unmodified corn (1) and potato (2) starches. Arrows point to the extrapolated values for the critical concentrations.

The following relations represent the results within the range of concentration investigated:

Corn starch	$\eta = 1.07 (c - 1.9) + 1$
Potato starch	$\eta = 0.71 (c - 0.45) + 1$
Generalized	$\eta = K_1 (c - c_K) + 1$

where c_K is the critical concentration and K_1 is a constant depending on the properties of the suspended granules. Substituting this value for η in Equation (5), the following is obtained:

$$\eta = K \frac{p K_1 (c - c_K) + 1}{F} \quad (c \geq c_K).$$

The linear relation expressing laminar flow is obtained when $c = c_K$.

Viscosity-Concentration Relations in Lyophilic Sols Generally

On the basis of a large amount of evidence, both chemical and physical, obtained from different points of view, the lyophilic colloids such as rubber, proteins, cellulose derivatives, starches, etc., may be considered as long-chain "macro-molecules." These long thread-like molecules are composed of a large number of units joined together by primary valences. Lyophilic colloids show extraordinarily high viscosities in solution at relatively low concentration, and this was formerly generally ascribed to a large solvation, or static binding of the solvent. In the cases of lyophilic colloids that contain groupings such as $-\text{OH}$ and $-\text{CONH}-$, it is to be expected that such long-chain molecules will be able to bind appreciable quantities of solvent statically, but in such compounds as rubber, containing no such groupings, the high viscosity shown cannot be ascribed to this cause. Two explanations have been put forward, based on differing conceptions of the form which these molecules take in solution.

These long-chain molecules are regarded by Staudinger (22, pp. 516-519) as being straight and rigid, stretched out to their maximum possible length in solution. Such molecules are assumed to rotate, so that the effective volume of each molecule is that of a very short cylinder encompassing the rotatory movement. Under these assumptions the effective volume occupied by the molecule must be proportional to the square of the chain length. As has been pointed out by Haller (9), however, the above conception has entirely neglected the free rotatability of the primary valence bonds, and also the less important flexibility of these valence linkages. This freedom of rotation, together with the accepted conception of valency angles, leads directly to the conclusion that these long-chain molecules may assume a variety of bent, rolled up and tangled forms in solution. The flexibility of these valence linkages leads to the conception of a continual change of form of these molecules.

The extraordinarily high viscosity of lyophilic solutions is explained by Staudinger on the basis of the effective volume occupied by straight rigid molecules, and the steep increase of viscosity with concentration on the basis of the phase-volume ratio, if the effective volume of the dispersed phase is considered as being the total volume of the cylinders described above. Below the concentration at which the total volume of these cylinders becomes equal to the volume available, the system is termed a "sol-solution," while at higher concentrations the system is termed a "gel-solution." Thus a critical concentration is involved based on this conception of the effective volume occupied by the dispersed phase. Empirically Staudinger (22, pp. 516-519) has found for lower members of polymeric series that

$$\frac{\eta_{sp}}{c} = KM,$$

where M = mol. wt. of the compound. This relation has been extrapolated to the longer chain compounds. The molecular weight calculated for crude Hevea rubber by this means was found to be 170,000. From this was calculated the number of molecules in unit volume of a solution of a standard concentration. The effective volume of each molecule was calculated (on the basis of effective cylinders) to be $3.0 \times 10^8 \text{ \AA}^3$, using 4.5 \AA and 3.0 \AA as the length and maximum breadth of an isoprene unit respectively. This leads to a critical concentration of 0.095% for crude Hevea rubber. The writer has shown elsewhere (6) that the critical concentration by actual measurement is higher than 0.19%. In another of a voluminous series of publications on this subject (21) the effective volume of each molecule was calculated by Staudinger to be $1.5 \times 10^8 \text{ \AA}^3$ for the same molecular weight: this leads to a calculated critical concentration of 0.2%. The latter figure was apparently obtained by considering a double chain, *i.e.*, bent back on itself, and the cross section of the assumed cylinder assigned twice its previous value. The reason for assuming a double chain is not immediately apparent. It is difficult to understand also at what chain length in a polymeric series this doubling occurs, since the lowest members are considered as straight-chain compounds.

In the present instance, a series of measurements was made on a fairly highly converted dextrin. The critical concentration was found to be about 45-46%, *i.e.*, the effective volume described in another section is approximately 2.2 cc. The specific viscosity was measured at concentrations below the critical, and $\frac{\eta_{sp}}{c}$ was found to be approximately 1. This relation when plotted in Fig. 3 was found to be in fairly good agreement with comparable relations for swollen starch granules. Since the dispersed phase in starch pastes is known to consist of somewhat irregularly shaped granules, approximating somewhat to the spherical, it is probable that the dextrin, which is in solution and does not form a heterogeneous system in the ordinary sense, is also of approximately the same form.

The molecular weight of this dextrin was determined cryoscopically in water and found to be 2,264, *i.e.*, the molecule contains on the average 14 glucose residues. Using the same values as Staudinger, *viz.*, 5.2 Å and 7.5 Å for the length and maximum breadth of each unit respectively (23), the writer has calculated the effective volume of 1 gm. of this dextrin, on the basis of the cylinder of Staudinger, to be 8.35 cc. The critical concentration should therefore be 12% compared with the 45-46% determined experimentally. It has been noted indeed by Staudinger (22, pp. 75-76) that the starch molecule probably is an exception to his general rule in that it has an irregular form, thus distinguishing it from cellulose.

The writer tends rather to agree with the conception of Haller, that the lyophilic colloids are very long thread-like molecules, and, in solution, owing to freedom of rotation of the valency linkages, assume an irregular tangled form. It is probable that on the average the form approximates to a sphere, and that the effective volume, and hence the viscosity, is inordinately large owing to immobilization of solvent within such molecules. Systems such as emulsions are generally regarded as heterogeneous, whereas true solutions are regarded as homogeneous. It appears probable that lyophilic colloids are to be regarded as being definitely diphasic and similar in properties in many respects to emulsions. The discontinuous phase is very highly dispersed and each particle of dispersed phase is extremely deformable. The viscosity probably depends on volume relations alone, as is the case in other diphasic systems (14). At very low concentrations there is a very small increase in viscosity per unit concentration, the small increase being due probably to the residual structure discussed above. The flow is of the laminar type. When the phase-volume relation is such that insufficient volume is available for cross section of free flow, the viscosity rises very greatly. Owing to the extreme ease of deformation of such loosely built particles, enormous decreases in viscosity are obtained with increasing rate of shear. The structure found in these sols is dependent on the phase-volume relations and ease of deformation of the dispersed phase. It is quite possible that the volume encompassed by the loosely built form suggested for these long-chain molecules approaches the microscopic in dimensions, but owing to refractive index considerations,

even in the ultra-microscope, only a comparatively faint Tyndall cone is seen. Such phenomena as gelation at low concentrations, thixotropy, protective action, etc., are given a readily understandable physical basis with this conception. Further investigation of these relations in lyophilic sols is planned.

Experimental

The viscosities of aqueous pastes of the starches and dextrin and the fluidities of alkaline pastes of the starches were determined as previously described (6, 7). Molecular weight determination of the dextrin was carried out cryoscopically in water in 10 and 15% concentration. The results obtained were 2,287 and 2,240, average 2,264 (corrected for moisture content of the dextrin). The error due to impurities is low, the ash content of the dextrin being 0.03%.

Acknowledgment

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References

1. ARRHENIUS, S. *Biochem. J.* 11 : 112-133. 1917.
2. EINSTEIN, A. *Ann. Physik*, 19 : 289-306. 1906.
3. EINSTEIN, A. *Ann. Physik*, 34 : 591-592. 1911.
4. FARROW, F. D. and LOWE, G. M. *J. Text. Inst.* 14 : 414-440. 1923.
5. FREUNDLICH, H. *Colloid and capillary chemistry* (Translation from 3rd German Edition), E. P. Dutton and Co., New York.
6. GALLAY, W. *Can. J. Research*, 7 : 671-676. 1932.
7. GALLAY, W. and BELL, A. C. *Can. J. Research, B*, 14 : 360-372. 1936.
8. GALLAY, W. and BELL, A. C. *Can. J. Research, B*, 14 : 381-390. 1936.
9. HALLER, W. *Kolloid-Z.* 56 : 257-267. 1931.
10. HARRISON, W. *J. Soc. Dyers and Colorists*, 27 : 84. 1911.
11. HATSCHEK, E. *Kolloid-Z.* 7 : 301-304. 1910.
12. HATSCHEK, E. *Kolloid-Z.* 8 : 34-39. 1911.
13. HATSCHEK, E. *Kolloid-Z.* 27 : 163-165. 1920.
14. HATSCHEK, E. *Colloid chemistry* (Alexander). Vol. I. Chem. Cat. Co., New York. 1926.
15. HESS, W. R. *Kolloid-Z.* 27 : 1-11. 1920.
16. OSTWALD, W. *Kolloid-Z.* 68 : 211-226. 1934.
17. SAKURADA, I. *Kolloid-Z.* 63 : 311-315. 1933.
18. SECK, W. *Kolloid-Z.* 64 : 86-91. 1933.
19. SIBREE, J. O. *Trans. Faraday Soc.* 26 : 26-36. 1930.
20. SIBREE, J. O. *Trans. Faraday Soc.* 27 : 161-176. 1931.
21. STAUDINGER, H. *Kautschuk*. 6 : 153-158. 1930.
22. STAUDINGER, H. *Die hochmolekularen organischen Verbindungen*, Verlag von Julius Springer, Berlin. 1932.
23. SPONSLER, O. L. and DORE, W. H. *Colloid Symp. Mono.* 4 : 174-202. 1926.
24. TREVAN, J. W. *Biochem. J.* 12 : 60-71. 1918.

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXVIII. THE BEHAVIOR OF LIGNIN TOWARDS ACTIVATED HYDROGEN¹BY R. G. D. MOORE² AND HAROLD HIBBERT³

Abstract

Methylated methanol lignin prepared from fully methylated spruce wood-meal was subjected, at relatively low temperatures and pressures, to the action of hydrogen in the presence of catalysts, and under conditions such that reduction of open-chain ethylenic linkages readily occurs. Entirely negative results were obtained. This pointed to the absence of ethylenic linkages in the lignin building unit.

Introduction

The presence of ethylenic linkages in lignin has not been definitely established. While Hibbert and Sankey (15) have advanced evidence indicating that bromine adds to lignin, the reaction being accompanied by substitution, Freudenberg and co-workers maintain that with halogens, substitution is the only reaction, and that no positive proof of the existence of a typical olefinic link in lignin has been given. Nevertheless both of the above-mentioned workers (10, p. 127; 13) found that lead tetra-acetate reacted with lignin to a slight extent. This indicated the presence of a maximum of one ethylenic linkage for every eight methoxyl groups.

The few recorded attempts to reduce lignin catalytically have yielded uniformly negative results. A. von Wacek (16) employed as catalyst palladium absorbed on barium sulphate, using both acetone and acetic acid as solvents, and found that no absorption of hydrogen occurred at atmospheric pressure. At somewhat higher pressures and temperatures, with cyclohexanol or acetic acid as solvent, dark colored products with a lower methoxyl content were obtained. Fierz-David (9) distilled lignin with a nickel catalyst in hydrogen at pressures as high as 100 atm. The conditions were actually those of a Bergius distillation, and not to be compared with a high pressure catalytic reduction as carried out by Adkins and co-workers (2, 3, 7, 8). Various fractions were obtained but not identified. Similar results were obtained by Bowen and Nash (4), using alumina or nickel oxide as catalyst. Recently Freudenberg (12) subjected lignin sulphonic acid to the action of hydrogen at 230° C. and 250 atm. pressure, using a nickel catalyst, but no definite results were obtained.

The existence of ethylenic linkages, or keto groups in conjugation with a benzene ring, is not supported by the work of Herzog and Hillmer (14) on absorption spectra.

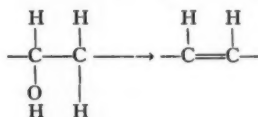
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The possibility of a "latent" double bond has been advanced (10, pp. 127-128) to account for the above negative results obtained by halogenation and reduction, as well as to explain the formation of lignin sulphonic acid. The unsaturated linkage is assumed not actually to exist in lignin, except in a minor degree, but to be formed by a reaction involving elimination of water:



In the present investigation an examination was made of the action of hydrogen on methylated methanol lignin in the presence of more recently developed catalysts (1, pp. 53-59 and 452-458; 7). The lignin used was prepared from fully methylated spruce wood-meal by a method analogous to that described by Hibbert and co-workers (5, 6). As catalysts Adams' reduced platinum oxide (1, pp. 452-458) and Raney nickel (7) in suspension in ethanol or glacial acetic acid were employed, both at room temperature and at 55-60° C., with a hydrogen pressure of 45 lb. per sq. in. Several variations in procedure, such as pre-reduction of the platinum catalyst, were tried, but in all cases the absorption of hydrogen was the same both in the presence and in the absence of the methylated lignin. The catalyst was shown to have retained its full capacity for reduction, hence the lignin did not act as a catalyst poison, and in addition could be recovered quantitatively with unchanged methoxyl content.

Fully methylated methanol lignin therefore possesses no characteristic open-chain ethylenic linkage reducible by hydrogen under the conditions employed. The sensitivity of the method was sufficient to permit the detection of a single unsaturated linkage in a product with a molecular weight of 1000-1500.

Experimental

The special reduction apparatus described by Adams (1, pp. 53-59) was used with modifications. Since it was necessary to deal with small amounts of material, the pressure tank was used for storage purposes only, and the pressure gauge was attached to the shaking bottle with taped, thick walled rubber tubing.

The lignin used was prepared from spruce meal, fully methylated with dimethyl sulphate and alkali, by heating with anhydrous methanol and hydrogen chloride under pressure. The methylated lignin obtained was again treated with dimethyl sulphate and alkali, with the object of obtaining a fully methylated methanol lignin. The product (OCH₃, 34-35%) proved not to be homogeneous and was fractionated by the following procedure: (i) the dioxane solution was precipitated slowly into ether; (ii) the residue obtained by evaporation of this mother liquor was dissolved in benzene and precipitated into ether; (iii) the concentrated mother liquor was precipitated

into petroleum ether, b.p. 30–50° C. The methoxyl contents of the three fractions from a representative experiment were respectively 32.5, 33.2 and 35.6%.

EXPERIMENTS WITH PLATINUM AS CATALYST

The hydrated platinic oxide was prepared according to Adams' method (1, pp. 452–458), and the activity of the catalyst shown by a reduction of diethyl maleate in ethanol (95%).

Method

The material to be reduced was dissolved in 200 cc. of solvent, 0.100 gm. of catalyst added, the apparatus evacuated, swept out with hydrogen, and placed under a hydrogen pressure of 45 lb. per sq. in. After five minutes, in order to obtain equilibrium conditions, the pressure was readjusted to the above pressure, the temperature inside the protecting cover of the bottle recorded, and shaking started. Pressure readings were taken at appropriate intervals, governed by the rate of reduction. A decrease in pressure of approximately 15 lb. per sq. in. was caused by 0.01 mole (1.721 gm.) of diethyl maleate. The pressure drop due to solution of hydrogen and reduction of the platinic oxide in an ethanol medium was found to be 5 lb. per sq. in. in two hours.

With 1.000 gm. of methylated methanol lignin (OCH_3 , 35.5%) in ethanol (95%), the pressure decrease was only 5 lb. per sq. in. in two hours. This indicated no absorption. The lignin was recovered quantitatively by the usual methods (concentration, precipitation into water, purification by precipitation from benzene or dioxane solution into low boiling petroleum ether) and was unchanged in external appearance and methoxyl content (found: 35.5% OCH_3).

When the catalyst was reduced with hydrogen prior to the introduction of the lignin similar results were obtained. With a lignin of lower methoxyl content (32.2%) negative results were also obtained. The retention of activity by the catalyst was indicated by its pyrophoric properties after filtration from the lignin solution. Preliminary addition of hydrazine hydrate to reduce the platinum oxide did not affect the results.

Glacial acetic acid was then tried as a solvent, both at room temperature and at 55–60° C. with similar negative results. The observed decrease in pressure, after preliminary reduction of the catalyst, was 2.0 ± 0.2 lb. per sq. in. irrespective of whether the methylated lignin (1 gm.; OCH_3 , 33.6%) was present or not.

EXPERIMENTS WITH RANEY NICKEL AS CATALYST (7)

This catalyst was prepared from the nickel-aluminium alloy according to the directions of the manufacturers (13), and kept under ethanol (95%). Its activity was shown by its highly pyrophoric property and by its rapid reducing action on diethyl maleate. About 1 gm. of the catalyst was used, the exact weight being determined by removing the ethanol under reduced pressure

and weighing in an atmosphere of nitrogen. The solvent used was glacial acetic acid at room temperature. Although the formation of nickel acetate occurred to some extent, as shown by the green color of the solution, this did not affect the catalytic activity of the residual nickel.

On shaking the catalyst suspension (containing 1.003 gm. of catalyst) in 200 cc. of glacial acetic acid (purified with permanganate and acetic anhydride) under a hydrogen pressure of 45 lb. per sq. in., the observed decrease in pressure was 1.9 lb. per sq. in. in 13 min. When 1.000 gm. of lignin (OCH_3 , 33.8%) was added, the observed pressure decrease was 2.1 lb. per sq. in. in the same period, with a further drop of 0.5 lb. per sq. in. at the end of 90 min. These results were duplicated in a second experiment. The residual catalyst possessed undiminished activity even after prolonged shaking with the lignin solution, as shown by the addition of 0.01 mole (1.721 gm.) of diethyl maleate. Shaking for 15 min. at an initial pressure of 45 lb. per sq. in. was sufficient to bring about complete reduction of the ester. Additional evidence as to the activity of the catalyst was supplied by its spontaneous ignition when exposed to the air after removal of the acetic acid.

References

1. ADAMS, R. and VOORHEES, V. Organic syntheses, Collective Vol. I. J. Wiley & Sons, New York. •1932.
2. ADKINS, H. Ind. Eng. Chem. Anal. Ed. 4 : 342-345. 1932.
3. ADKINS, H. J. Am. Chem. Soc. 55 : 4272-4275. 1933.
4. BOWEN, A. R. and NASH, A. W. Fuel Science Practice, 5 : 138-142. 1926.
5. BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 28-34. 1935.
6. COMPTON, J., GREIG, M. and HIBBERT, H. Can. J. Research, B, 14 : 115-119. 1936.
7. COVERT, L. W. and ADKINS, H. J. Am. Chem. Soc. 54 : 4116-4117. 1932.
8. COVERT, L. W., CONNOR, R. and ADKINS, H. J. Am. Chem. Soc. 54 : 1651-1663. 1932.
9. FIERZ-DAVID, H. E. and HANNIG, M. Helv. Chim. Acta, 8 : 900-923. 1925.
10. FREUDENBERG, K. Tannin, Cellulose, Lignin. J. Springer, Berlin. 1933.
11. FREUDENBERG, K., BELZ, W. and NIEMANN, C. Ber. 62 : 1554-1561. 1929.
12. FREUDENBERG, K., SOHNS, F. and JANSON, A. Ann. 518 : 62-85. 1935.
13. GRAY, K. R., BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 48-54. 1935.
14. HERZOG, R. O. and HILLMER, A. Ber. 60 : 365-366. 1927.
15. HIBBERT, H. and SANKEY, C. A. Can. J. Research, 4 : 110-118. 1931.
16. WACEK, A. VON. Ber. 63 : 282-296. 1930.



